400. *Heterocyclic Derivatives of Guanidine. Part II.*[1] *Some Derived Products.*

By J. E. Banfield.

Cyclisation of 2-(α-cyano-α-ethoxycarbonylmethylene)-5-oxo-3,4-diphenyl-3-pyrroline (I) gave ethyl 3-amino-4-(α-ethoxycarbonylbenzylidene)-1,4-dihydro-1-imino-2-naphthoate (II) with ethyl 3,5-dihydro-5-imino-2-oxo-1-phenyl-2*H*-benz[*e*]indole-4-carboxylate (III) as a by-product. Some derivatives of these products are described.

In an analogous reaction, 2,5-di-(α-cyano-α-ethoxycarbonylmethylene)-3,4-diphenyl-3-pyrroline (VIII) gave diethyl 7,9-dihydro-5,9-di-imino-5*H*-dibenzo[*c*,*g*]carbazole-6,8-dicarboxylate (IX).

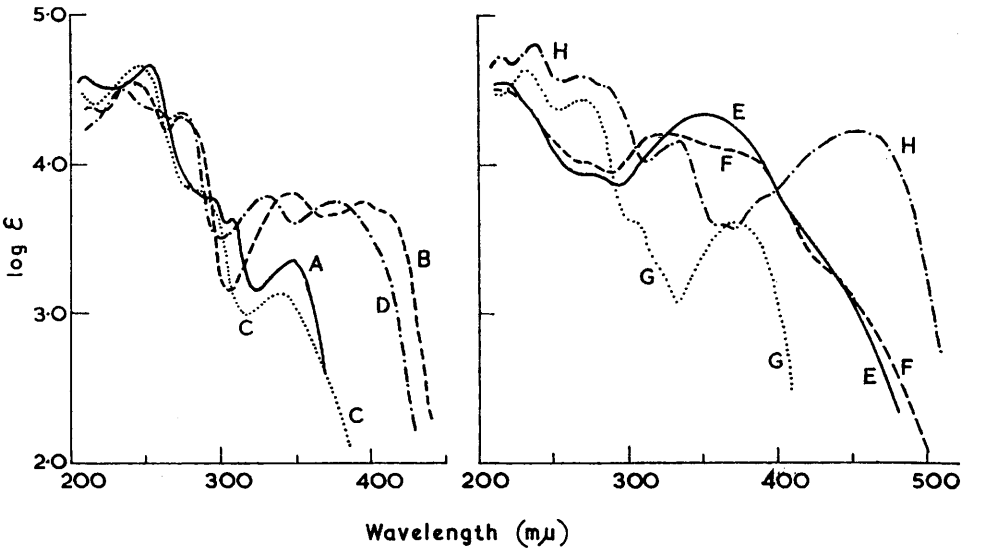
Reaction of ethyl cyanoacetate with 5-guanidino-2-imino-3,4-diphenyl-2*H*-pyrrole and with 2-imino-3,4-diphenyl-5-oxo-3-pyrroline, the latter readily obtained from the former compound, readily provides compounds (VIII) and (I) respectively.[1] The reported cyclisation of *trans*-αβ-dicyanostilbene in sulphuric acid to 3-cyano-2-phenylinden-1-one [2] (an imino-group being lost by hydrolysis) led to the suggestion that the esters (I) and (VIII) might be cyclised similarly.

Reaction of the ester (I) with sulphuric acid gave, unexpectedly, a low yield of a compound of constitution corresponding to the addition of ethanol (which was not lost on sublimation and was presumably provided by a disproportionation); higher yields were obtained when ethanol was isothermally distilled into the reaction mixture. This compound lacked absorption at *ca.* 2200 cm.$^{-1}$. Its ultraviolet absorption (Fig. 1B), being bathochromically and hypochromically displaced from that of the precursor (I), is consistent rather with a cyclic than with an imino-ether structure. It contained two ethoxyl groups (although slightly low ethoxyl values were obtained consistently), both of which were lost on saponification. The genesis of the second ester group can be ascribed to ethanolysis of the lactam group of (I), amides being readily hydrolysed by a unimolecular mechanism under similar conditions.[3] Thus the product is the quinone-imine (II), a structure which is consistent with the spectral change on reductive acetylation (Fig. 1B ⟶ A). The ultraviolet absorption of the reductive acetylation product was of naphthalenic type, although at rather longer wavelengths than usual. However, ethyl

[1] Part I, *J.*, 1960, 2108.
[2] Coe, Gale, Linstead, and Timmons, *J.*, 1957, 123.
[3] Duffy and Leisten, *J.*, 1960, 856.

1,3-diamino-2-naphthoate, known as a product of an analogous cyclisation of ethyl α-cyano-β-imino-γ-phenylbutyrate, is bright yellow.[4] In our hands this base readily yielded a monoacetyl derivative, formulated as ethyl 3-acetamido-1-amino-2-naphthoate, in acetic anhydride at moderate temperatures. This derivative was pale yellow and its ultraviolet absorption (Fig. 1D) resembled somewhat that of the amine (II), although this resemblance is considered fortuitous; it is noteworthy that the colour of 2-hydroxyacetophenone has been ascribed to chelation.[5] This monoacetyl derivative was further acetylated by keten, to give a triacetyl derivative; *C*-acylation being considered unlikely and a band at 870 cm.$^{-1}$ being present (possibly pentasubstituted aromatic), the latter is formulated as ethyl 3-acetamido-1-diacetylamino-2-naphthoate, 2·6 mol. of acid being obtained in an

FIG. 1. FIG. 2.



FIGS. 1—2. *Ultraviolet absorption spectra.*

A, *Compound* (IV; R = H); max. at 348, 308, 296, 253, 215 mμ (log ε 3·359, 3·635, 3·768, 4·663, 4·546). B, *Compound* (II); max. 394, 347, 274, 240 mμ (log ε 3·756, 3·808, 4·324, 4·553). C, *Ethyl 3-acetamido-1-diacetylamino-2-naphthoate*; max. 338, 286, 247 mμ (log ε 3·140, 3·838, 4·662). D, *Ethyl 3-acetamido-1-amino-2-naphthoate*; max. 377, 331, 273, 234 mμ (log ε 3·750, 3·788, 4·348, 4·513). E, *Compound* (III); max. 350, 273, 216 mμ (log ε 4·335, 3·940, 4·541). F, *Compound* (V); max. 327, 272, 214 mμ (log ε 4·205, 4·019, 4·501). G, *Compound* (VII); max. 372, 270, 232 mμ (log ε 3·614, 4·440, 4·623). H, *Compound* (IX); max. 447, 362, 334, 285, 268, 237, 214 mμ (log ε 4·215, 3·600, 4·163, 4·515, 4·593, 4·804, 4·723).

N-acetyl determination. Although having strong ν(NH) absorption in the infrared region, this compound had no active hydrogen in the Zerewitinoff determination (MgMeI in anisole at 95°). Its ultraviolet absorption (Fig. 1C) closely resembled that of the reductive acetylation product of (II) which is formulated (see below) as (IV).

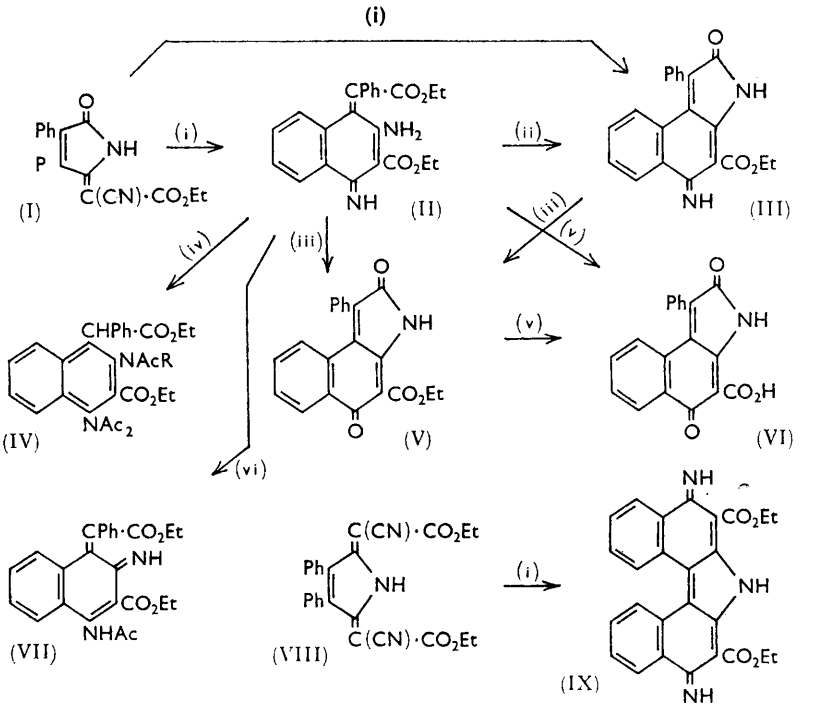
Although the amine (II) decomposed extensively at 230°, and it was recovered from refluxing diphenyl ether, a trace of sodium in this solvent converted it into the lactam (III), which was also obtained as a minor product of the cyclisation of the nitrile (I). Hot acetic acid converted both the amine (II) and the imino-lactam (III) into the oxo-lactam (V) and both this and the amine (II) were hydrolysed by ethanolic sodium hydroxide to the acid (VI). The ultraviolet absorption of the keto-lactam (VI) (Fig. 2F) and the imino-compound (III) (Fig. 2E) differed but in detail and were generally similar to that of both

[4] Atkinson and Thorpe, *J.*, 1906, **89**, 1920.
[5] Crawford and Supanekar, *J.*, 1960, 1985.

the acid (VI) and, to a smaller extent, the ester (II). The absorption of the imino-compound (III) in ethanol was changed by either acetic or perchloric acid and it then somewhat resembled that of the amine (II) the absorption of which was only slightly altered by acid. The amine (II) with keten gave an acetyl derivative the elementary composition of which was more consistent with that of a monoacetyl than a diacetyl derivative, an *N*-acetyl determination giving *ca.* 1 mol. of acid; the *o*-quinone imine structure (VII) is preferred on spectral grounds—mainly the absence of $\nu(NH_2)$ symmetrical and asymmetrical bands at *ca.* 3400 and 3500 cm.$^{-1}$, and its ultraviolet absorption (Fig. 2G).

The bis-ester (VIII) was cyclised by sulphuric acid to its isomer (IX) the structure of which follows from its lack of C:N absorption and from the position of its ultraviolet absorption (Fig. 2H) relative to that of the parent compound (VIII); however, a tautomeric amino-structure also merits consideration for this compound.

The infrared absorption of the above compounds displayed some unexpected features. It is apparent that a doublet at 1680—1693 cm.$^{-1}$ of the ester (VIII) and a band at 1665 cm.$^{-1}$ of compound (IX) are due to αβ-unsaturated ester modes, the latter frequency being



(i) H_2SO_4. (ii) Na–Ph_2O. (iii) AcOH. (iv) Ac_2O–Zn. (v) KOH–EtOH. (vi) CH_2:CO.

lowered by hydrogen bonding. Data for CO·NH in a five-membered unsaturated ring of the above type are not abundant; however, by analogy with δ-lactams (1665 cm.$^{-1}$) and unsaturated δ-lactams (1675 cm.$^{-1}$),[6] this group might be expected to absorb at somewhat higher frequencies than γ-lactams (1700 cm.$^{-1}$);[6] a band at 1749 cm.$^{-1}$ has previously[1] been attributed to such a function in 5-*NN*-dimethylguanidino-2-oxo-3,4-diphenyl-2*H*-pyrrole nitrite. Thus the 1749 cm.$^{-1}$ band of the nitrile (I) can be ascribed to a ν(CO·NH) mode and hence the 1708 cm.$^{-1}$ band to the unsaturated ester function.

[6] R. N. Jones and Sandorfy, in Weissberger, "Techniques of Organic Chemistry, Vol. IX. Chemical Applications of Spectroscopy," Interscience, Publ. Inc., New York, 1956, pp. 458—535.

For diphenylmaleinimide the doublet at 1764 and 1711 cm.$^{-1}$ is apparently due to this mode, the average frequency (1738 cm.$^{-1}$) possibly being raised somewhat by coupling due to dipole interaction; and for 2-imino-3,4-diphenyl-5-oxo-3-pyrroline, bands at 1729 and 1706 cm.$^{-1}$ are probably (CO·NH) modes split by interaction with the C=NH function. Accordingly strong bands at 1722, 1732, and 1735 cm.$^{-1}$ of compounds (III), (V), and (VI), respectively, are readily recognisable as due to this function, other bands in this region being displaced appropriately as the other functional groups are altered.

For ethyl 3-acetamido-1-amino-2-naphthoate the assignments 3488 [$\nu(NH_2)$ asym.], 3370 [$\nu(NH_2)$ sym.], 3220, 3138 [$\nu(NH)$], 1657 (aromatic ester, bonded), 1631 (NHAc),[7,8] 1610 [$\delta(NH_2)$],[9] and 1553 cm.$^{-1}$ (Amide II) [7] seem reasonable, and for ethyl 3-acetamido-1-diacetylamino-2-naphthoate, absorption at 3348 [$\nu(NH)$], 1680 [$\nu(NHAc)$],[8] 1601 (aromatic C=C), and 1522 cm.$^{-1}$ (Amide II) is in accord with expectation. Data for aromatic secondary amides have been reviewed; [10] two or three bands, depending upon the resolution, appear in the 1690—1730 cm.$^{-1}$ region. Thus *NN*-diacetylaniline absorbs at 1724, 1712, and 1701 cm.$^{-1}$; *NN*-diacetyl-*o*-anisidine at 1728, 1720, and 1704 cm.$^{-1}$; and *NN*-diacetyl-1-naphthylamine at 1727 and 1706 cm.$^{-1}$. Thus it is likely that the secondary amide bands of the triacetyl derivative contribute to the broad and asymmetrical peak at 1710 cm.$^{-1}$ with a shoulder at 1721 cm.$^{-1}$ and an inflection at 1703 cm.$^{-1}$ which must also include the peak expected for the CO_2Et group.

Analyses for the reductive acetylation product from compound (II) indicated a tetra-acetyl or, slightly more probably, a triacetyl derivative, and the compound gave 2—3 mol. of acid in the usual *N*-acetyl determination; but, in view of the low values for some of the above compounds, this is not considered to exclude definitely the tetra-acetyl formulation; results of the active hydrogen determination might be accounted for by the active ethyl diarylacetate hydrogen. Although both ethyl 3-acetamido-1-diacetylamino-2-naphthoate and compound (IV) had somewhat similar absorption in the 1570—1630 cm.$^{-1}$ region, and both absorbed strongly between 1690 and 1740 cm.$^{-1}$, the peaks of this product in the latter range were at quite different positions from those of the simpler analogue; this suggested the alternative formulation of it as the tetra-acetyl compound (IV; R = Ac) which would explain not only the above differences, but also the lack of specific absorption in the NH region, and the lack of a band in the 1500—1650 cm.$^{-1}$ region of a strength expected for an Amide II band; in this case the peak at 1705 cm.$^{-1}$ could be assigned to the secondary amide functions and the peak at 1730 cm.$^{-1}$ to these together with absorption of the unbonded ring ester function. The strong peak at 1786 cm.$^{-1}$ of this compound must be due to the aliphatic CO_2Et group, its frequency being extraordinarily high.

The acetyl derivative (VII) absorbed at 1750 cm.$^{-1}$, again an exceptionally high frequency for, in this case, an αβ-unsaturated ester; absorptions at 3384, 3210 [$\nu(NH)$], 1713 (CO_2Et, aromatic), 1687 (NHAc), 1661 cm.$^{-1}$ (C=N), and 1529 cm.$^{-1}$ (broad) (Amide II) account for the absorption expected in this region for the other functions. There is, in fact, a far closer resemblance between the infrared absorption of ethyl 3-acetamido-1-diacetylamino-2-naphthoate and the acetyl derivative (VII), than between the former and the reductive acetylation product (IV), further raising the possibility that the product (VIII) was in fact a diacetyl derivative. In an attempt to clarify this point this acetyl compound was refluxed in acetic acid in the expectation that cyclisation with loss of ethanol would occur should the β-amino-function not be protected, as in the reaction of compound (II) with this reagent; in the event the acetyl compound was recovered, and its analysis was then unambiguous for the monoacetyl derivative of compound (II). Failure under these conditions to hydrolyse an α-imino-function, or to cyclise the lactam ring at

[7] Gerrard, Lappert, Pyszora, and Wallis, *J.*, 1960, 2144, where mention is made of large shifts of amide I and II bands (complementary) with intermolecular association.
[8] Katritzky and Jones, *J.*, 1959, 2067.
[9] Katritzky and Jones, *J.*, 1959, 3674.
[10] Abramovitch, *J.*, 1957, 1414; see also Cramer and Baer, *Chem. Ber.*, 1960, **93**, 1231.

the β-nitrogen atom, of this compound seems inconsistent either with an α-acetimido-β-amino-structure or a β-acetamido-α-imino-structure and thus the α-acetamido-β-imino-structure (VII) is further supported. Further, an attempt to hydrolyse the acetyl compound under conditions comparable to those of the *N*-acetyl determination, in which the evolution of (probably) ammonia was noted, gave an acidic product clearly different from the acid (VI). This result seems inexplicable unless hydrolysis of the β-imino-group of compound (VII) to a keto-group is faster than that of the α-acetamido-group. Owing to difficulties in the purification of this saponification product no satisfactory analytical evidence in support of this rationalisation is presented; the structure of this acidic product is, in any case, largely incidental to the above argument.

Prolonged acetylation of compound (II) by keten gave a benzene solvate of the diacetyl derivative which must be formulated as the α-diacetylamino-compound as it was hydrolysed by acetic acid to the monoacetyl compound (VII), secondary amides being known to hydrolyse under these conditions. Although the formation of diacylamines is known to be assisted by the presence of groups adjacent to the amino-function, their formation by the action of keten on aromatic amines is apparently without precedent; neither α- nor β-naphthylamine gave the diacyl derivative under comparable conditions.

The amine (II) has negligible absorption above 1730 cm.$^{-1}$ in the C=O region, and thus the two strong peaks at 1717 and 1677 cm.$^{-1}$ must be due to the two ester functions, both of which may be strongly bonded to adjacent NH or NH_2 groups with consequent reduction in frequency, as in methyl *N*-methylanthranilate,[11] and in the above-mentioned ethyl acetamido-1-amino-2-naphthoate [ν(C=O) not above 1673 cm.$^{-1}$].

Absorption is characteristically strong for the exocyclic C=C function as in compounds (VIII), (I), (II), and (VII); in most of the other compounds it is weak. Frequencies and some further empirical assignments of bands for some of the above compounds are given in the following list.

Spectra.—Frequencies (cm.$^{-1}$) and estimates of the intensities of the main absorption bands for Nujol mulls were estimated from spectra kindly determined by Dr. D. L. Ford, Timbrol Company, Sydney, whom we thank. A Perkin-Elmer model 21 double-beam spectrophotometer fitted with a rock-salt prism was used. Bands in the region of the main Nujol bands, unless very prominent, have been ignored.

Compound (VIII): 3294 (NH); 3034sh,m (arom. CH); 2225m (CN); 1693, 1680 (αβ-unsat. ester, split); 1610s, 1599s (C=C, exocyclic, split), 1563sh,m; 1274s (COCO, ester), 1204s, 1185s, 1165s, 1157, 1110, 1080s, 1070m, 1047s, 1032m, 1013sh, 1004s, 999sh,m, 940, 930, 856s, 775s, 752s, 725s, 700s, 690m.

Compound (IX): 3460m, 3396m, 3330m, (NH); 1665s (αβ-unsat. ester, bonded); 1604s (C=C, C=N); 1551m, 1520m (aromatic); 1316s (CO·CO, ester), 1274, 1250m, 1223s, 1178s, 1171s, 1143m, 1098m, 1085m, 1080m, 1034m, 1019sh, 943, 933, 789m, 756s, 743s, 699s.

Compound (I): 3360s (NH); 2239 (CN), 1749s, 1708asym,s; 1611s, 1600s (C=C, exocyclic, split), 1347m; 1260s (CO·CO, ester), 1176sh,s, 1160s, 1095m, 1089m, 1085m, 1060s, 1003, 968m, 853, 799, 783s, 767m, 761m; 699s [δ(CH), Ph].

Diphenylmaleinimide: 3157s, 3040s, 2722 (NH···O=C), 1764m, 1711s, 1600m, 1342s,asym., 1183, 1146m, 1080, 1072, 1033, 1021s, 950, 929, 848, 809, 775s, 757s, 742m, 708s, 689s.

2-Imino-3,4-diphenyl-5-oxo-3-pyrroline: 3306br, with absorption to 3000, 2744br,m (NH···O=C), 1729s, 1706s, 1661s, 1601m, 1416m, 1362s, 1207m, 1121m, 1071m, 1046m, 1025m, 861m, 856m, 834s, 797s, 767s, 754sh,m, 723s, 701s, 690s.

Ethyl 3-amino-4-(α-ethoxycarbonylbenzylidene)-1,4-dihydro-1-imino-2-naphthoate: 3445s, 3330s (NH_2, NH, bonded); 1717s, 1677s, (CO_2Et); 1614s [δ(NH_2), C=C]; 1603s, 1547, 1515 (arom.), 1437, 1390, 1325, 1310m; 1271s, 1246s (CO·CO, ester), 1227sh, 1175m, 1153m, 1134, 1108, 1084, 1078m, 1066m, 1047, 1021, 1008, 978, 889, 798m; 763s (*o*-disubst. arom.); 699s (Ph).

Compound (III): 3304m, with broad absorption to 2700 (NH and bonded NH); 1722s (CO·NH); 1687s (CO_2Et, bonded), 1672sh; 1612m, 1591m, 1572m (C=C, C=N); 1410, 1345,

[11] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 185.

1330, 1274, 1249, 1199, 1174, 1151, 1122, 1096, 1061, 1032, 1002, 977, 922, 802; 769m (*o*-disubst. arom.), 719; 708 (Ph).

Compound (V): 3380m (NH); 1732s, 1720sh (CO·NH, CO_2Et); 1670br,s, 1657sh (C=O); 1622m (C=C); 1599, 1568 (arom.), 1293m, 1272sh, 1230m, 1167, 1142, 1058, 1037, 969, 897; 774 (*o*-disubst. arom.), 739, 723; 705m (Ph–), 693.

Compound (VI): 3370m (NH); 2650br (OH, bonded); 1735s (CO·NH); 1709s,br (CO_2H); 1632s (C=O bonded to OH);[a] 1610m, 1594m, 1580m, 1557m, 1545sh (C=C, arom.); 1405s (CO_2H), 1364s, 1335, 1301s, 1208, 1151m, 1141sh, 1095, 1075, 1058, 1033, 1000, 961m, 897s, 884sh, 843, 818, 800m; 779s (*o*-disubst. arom.), 763, 750, 712m; 705s (Ph), 693m.

Compound (VII): 3384m, 3210m, 1750s, 1713s, 1687s, 1678sh, 1661s; 1629s (C=C), 1602, 1575m, 1529m,br, 1503m, 1400sh, 1334m, 1313m; 1284, 1266m, 1236s (CO·CO, ester), 1219sh, 1175s, 1158s, 1138m, 1124m, 1094s, 1073m, 1050, 1031, 1003, 974, 918, 887, 856, 834, 798, 765s; 748s (*o*-disubst. arom.), 729, 719; 698s (Ph).

Compound (IV): low-intensity broad absorption only in NH region; 1786s, 1730s, 1705s, 1677 infl., 1623; 1595, 1570, 1511 (arom.), 1420sh, 1317s, 1284m; 1237s, 1215sh (CO·CO, ester), 1195, 1185, 1160m, 1145, 1118, 1100, 1079, 1045, 1029, 1022, 1007, 973m, 950, 922, 896, 864, 818; 768s (*o*-disubst. arom.), 729m, 722; 696m (Ph).

Ethyl 3-acetamido-1-diacetylamino-2-naphthoate: 3348, 1721sh, 1710s, 1680m, 1658sh, 1630; 1601m, 1573 (arom.), 1522s, 1489m, 1341, 1331, 1309m, 1288m; 1264s (CO·CO, ester), 1231s, 1200sh, 1168, 1153m, 1142, 1119, 1093m, 1077, 1027, 1017m, 983m, 965sh, 909, 897; 870m (pentasubst. arom.), 860, 792s; 762s (*o*-disubst. arom.), 747sh, 719, 675.

Ethyl 3-acetamido-1-amino-2-naphthoate: 3488s, 3370s, 3220m, 3138s, 2700, 1673sh,m, 1657s, 1631s, 1610m, 1561m, 1553s, 1533m, 1502, 1437; 1345s (CO·CO, ester), 1302, 1276 1247m, 1232s, 1169s, 1143m, 1135sh, 1107, 1087s, 1019, 943, 896; 861m (pentasubst. arom.) 837m, 802s, 776sh; 771m (*o*-disubst. arom.), 743s, 724

[a] Cf. 1-hydroxyanthraquinones; ref. 6, p. 492.

Experimental

Ultraviolet absorption spectra were determined for 95% EtOH solutions on an Unicam S.P. 500 spectrophotometer by Mrs. J. E. Banfield, B.Sc. Identity of compounds which decomposed heavily on melting was in each case confirmed by the identity of their ultraviolet absorption (in addition to elementary analysis), mixed m. p. determination being of little value for compounds of this type.

Cyclisation of 2-(α-*Cyano*-α-*ethoxycarbonylmethylene*)-5-*oxo*-3,4-*diphenyl*-3-*pyrroline*.—(*a*) In a preliminary experiment the ester (I) (1·0 g.) was dissolved in sulphuric acid (7 ml.), and the mixture was set aside for 2 days and then poured into water. A red solid, probably a sulphate (0·84 g.), was deposited and this, recrystallised from aqueous ethanol and chromatographed in benzene on alumina (Spence " H," deactivated with 3% of 10% acetic acid), gave *ethyl* 3-*amino*-4-(α-*ethoxycarbonylbenzylidene*)-1,4-*dihydro*-1-*imino*-2-*naphthoate* (II) (0·31 g.), in pale yellow prisms (from ethanol), m. p. 255—258° (decomp.), 273° * (* here and below indicates a tube placed in the bath at 230°) (Found: C, 70·65; H, 5·8; N, 7·2; O, 16·7; OEt, 20·6. $C_{23}H_{22}N_2O_4$ requires C, 70·75; H, 5·7; N, 7·2; O, 16·4; 2EtO, 23·0%). The mother-liquors afforded a pale yellow solid (0·05 g.), m. p. 262—265° (decomp.), which sublimed at 230—235°/0·01 mm., giving a further quantity of the amine, m. p. 261—266° (decomp.), 271° * (Found: C, 70·7; H, 5·8; N, 7·2; O, 16·7; OEt, 20·5%).

The m. p. of the amine depended on the rate of heating; melting occurred at 230° after *ca.* 15 min. The compound was neutral to potentiometric titration with acid and with base in ethanol, and dissolved in concentrated hydrochloric acid but not appreciably in the 5N-acid.

(*b*) The ester (I) (2·75 g.) was kept in sulphuric acid (50 ml.) at room temperature for 24 hr., then ethanol was allowed to distil isothermally into the mixture. This (after 1 week) afforded to benzene the above amine (1·04 g.), m. p. 253° * (decomp.), and to ether a further quantity (407 mg.) of the amine, m. p. 257° * (decomp.), as thick lemon-yellow needles (Found: C, 70·5; H, 5·8; N, 7·0; O, 16·7; OEt, 19·8%). In subsequent preparations the cyclisation was carried out during 2 days, basification was with ammonia, and the precipitate was extracted (Soxhlet) with chloroform, chloroform eluting the amine, m. p. 254° * (decomp.) (1·69 g.), from alumina.

(*c*) *Isolation of ethyl* 3,5-*dihydro*-5-*imino*-2-*oxo*-1-*phenyl*-2H-*benz*[e]*indole*-4-*carboxylate* (III).—(i) In a condensation analogous to (*b*), when the isothermal distillation was prolonged for several weeks, a chloroform eluate gave material (1·14 g.) of m. p. 233—236° (decomp.), (from ethanol). This recrystallised from chloroform–ethanol; deep yellow prisms were first deposited and subsequently pale yellow needles began to separate. The crystallisation was interrupted at this point and the initial material [101 mg. of m. p. 226—230° (decomp.)], washed with chloroform and purified from ether–chloroform, afforded the orange-yellow *lactam* (74 mg.), m. p. 231—233° (decomp.) either in characteristic diamond-shaped prisms or in plates with bluntly pointed ends (Found: C, 73·2; H, 4·8; OEt, 11·6. $C_{21}H_{16}N_2O_3$ requires C, 73·2; H, 4·7; OEt, 13·1%). Further crystallisation from the ethanol–chloroform solution afforded the above-mentioned amine, m. p. 265° * (decomp.) (Found: C, 70·5; H, 5·8; OEt, 20·5. $C_{23}H_{22}N_2O_4$ requires C, 70·75; H, 5·7; 2EtO, 23·0%).

(ii) In a cyclisation analogous to (*a*), the mixture was poured into ice–sodium carbonate, giving a crude solid (0·22 g.), which, chromatographed on alumina, afforded a benzene eluate and an ether eluate; material from the latter sublimed at 190—210°/0·01 mm. and then crystallised from chloroform–ether, giving the lactam (21 mg.) in yellow plates, m. p. 234° (decomp.) (Found: C, 73·4; H, 4·8; N, 7·8. $C_{21}H_{16}N_2O_3$ requires N, 8·1%; cf. above). The benzene eluate decomposed extensively when sublimed at 240°; the residue, purified from chloroform–ether, afforded the lactam in orange-yellow rhombs (Found: C, 73·15; H, 4·7; N, 7·45; O, 15·4; OEt, 11·6. $C_{21}H_{16}N_2O_3$ requires O, 13·9%; cf. above).

Conversion of Ethyl 3-*Amino*-4-(α-*ethoxycarbonylbenzylidene*)-1,4-*dihydro*-1-*imino*-2-*naphthoate* (II) *into Ethyl* 3,5-*Dihydro*-5-*imino*-2-*oxo*-1-*phenyl*-2H-*benz*[e]*indole*-4-*carboxylate* (III).—The amine (II) (197 mg.) was refluxed for a short time in diphenyl ether, a trace of sodium was added, and the mixture was refluxed for 10 min., allowed to cool, and added to diethyl ether containing a little ethanol. The solid was collected and purified to give the lactam (48 mg.) in characteristic diamond-shaped plates, m. p. 233—235° (decomp.) (Found: C, 73·3; H, 4·8; N, 7·9; OEt, 12·6%).

When, however, the amine (211 mg.) was refluxed in diphenyl ether for 1·5 hr. it (92 mg.) was recovered [m. p. 268—270° * (decomp.)]; some darker material was also formed. Addition of ammonium chloride to this mixture gave similar results.

The amine (II) decomposed to a clear brown melt when kept at 230° under nitrogen for 20 min.; the dark brown gum did not give a crystalline product to ether–chloroform.

Ethyl 3,5-*Dihydro*-2,5-*dioxo*-1-*phenyl*-2H-*benz*[e]*indole*-4-*carboxylate* (V).—(a) Ethyl 3-amino-4-(α-ethoxycarbonylbenzylidene)-1,4-dihydro-1-imino-2-naphthoate (II) (350 mg.) in acetic acid was refluxed for 1·5 hr. Diluting the mixture with water gave, in quantitative yield, the *ester* in yellow rods (from aqueous acetic acid), m. p. 225—226° (Found: C, 73·1; H, 4·4; N, 4·2; O, 18·9; OEt, 9·6. $C_{21}H_{15}NO_4$ requires C, 73·0; H, 4·4; N, 4·1; O, 18·5; OEt, 13·0%).

The ester was also obtained in an unsuccessful attempt to convert the amine in acetic acid containing sodium acetate into a *p*-nitrophenylhydrazone; it had m. p. and mixed m. p. 226° (Found: N, 4·25%).

(b) Ethyl 3,5-dihydro-5-imino-2-oxo-1-phenyl-2*H*-benz[*e*]indole-4-carboxylate (28 mg.), in acetic acid, was refluxed for 1·5 hr. to yield the ester (22 mg.), m. p. and mixed m. p. 225—226°.

3,5-*Dihydro*-2,5-*dioxo*-1-*phenyl*-2H-*benz*[e]*indole*-4-*carboxylic Acid* (VI).—Ethyl 3-amino-4-(α-ethoxycarbonylbenzylidene)-1,4-dihydro-1-imino-2-naphthoate (II) (366 mg.) was refluxed in aqueous-ethanolic potassium hydroxide for 5 hr., to give the *acid* (from aqueous acetic acid) in red needles, m. p. 270° (decomp.) (218 mg.), which did not lose weight when dried at 150°/0·01 mm. (Found: C, 72·3; H, 3·4; N, 4·9; O, 20·1; OEt, Nil. $C_{19}H_{11}NO_4$ requires C, 71·9; H, 3·5; N, 4·4; O, 20·2%).

This acid (57 mg.), m. p. 271° (decomp.) and undepressed on admixture, was obtained similarly from ethyl 3,5-dihydro-2,5-dioxo-1-phenyl-2*H*-benz[*e*]indole-4-carboxylate (V) (0·2 g.).

Acetylation of Ethyl 3-*Amino*-4-(α-*ethoxycarbonylbenzylidene*)-1,4-*dihydro*-1-*imino*-2-*naphthoate*.—(*a*) The amine (II) (375 mg.) was saturated with keten during 0·5 hr. The mixture was set aside for 1 hr., and solvent was removed, giving the *acetyl derivative* (VII) (419 mg.), which separated from benzene–light petroleum in pale yellow needles, m. p. 256—259° (decomp.) [Found: C, 69·0, 69·0; H, 5·9, 5·5; N, 6·3, 6·6; O, 19·5; OEt, 18·1; Ac, 8·7 (Wenzel's H_2SO_4), 9·9 (methanolic NaOH 8, hr.; Dr. Zimmermann reported the formation of an alkaline distillate in this analysis); active H, 0·6. $C_{25}H_{24}N_2O_5$ requires C, 69·4; H, 5·6; N, 6·5; O, 18·5; 2EtO,

20·8; Ac, 10·0; 2H, 0·5. Calc. for $C_{27}H_{26}N_2O_6$: C, 68·3; H, 5·5; N, 5·9; O, 20·2; 2EtO, 19·0; 2Ac, 18·1%].

This derivative (258 mg.) was refluxed in acetic acid during 3 hr., then the mixture was diluted to turbidity with water, giving a solid (64 mg.). This was run in benzene on alumina from which chloroform eluted the acetyl derivative, m. p. 258—259·5° (from aqueous acetic acid) (38 mg.), of ultraviolet absorption identical with that of the original material (Found: C, 69·3; H, 5·6; N, 6·5; OEt, 17·6%).

(*b*) In another experiment the amine (II) (0·71 g.) in chloroform was saturated with keten during 4 hr.; evaporation and chromatography afforded a solid (0·46 g.) (from benzene), m. p. 180°, which (130 mg.), refluxed as above in acetic acid, yielded the acetyl derivative (68 mg.), m. p. 258° (Found: C, 69·45; H, 5·7; N, 6·5; OEt, 18·5; Ac, 5·2%). Recrystallisation (four times) of the solid from benzene–light petroleum failed to change the unsatisfactory melting behaviour, *viz.*, partial melting at 180°, resolidification and remelting in the 205—220° range, although the *benzene hemisolvate* of the diacetyl derivative was so obtained in homogeneous feathery pale yellow needles (Found: C, 70·3; H, 5·8; N, 5·7; OEt, 15·35; Ac, 9·1. $C_{27}H_{26}N_2O_6,\frac{1}{2}C_6H_6$ requires C, 70·2; H, 5·75; N, 5·45; 2EtO, 17·5; Ac, 16·7%), $\lambda_{max.}$ at 373, 270, 232 (infl. at 302) mμ (log ε 3·595, 4·458, 4·608, 3·65) (closely resembling the absorption of the monoacetyl derivative). The solvate (56·7 mg.) lost 3·8 mg. when dried at 185°/0·05 mm. (fused; drying at 160° for 1 hour caused a loss of only 1·5 mg.) (calc.: 4·3 mg.), to give *ethyl 4-diacetylamino-1-(α-ethoxycarbonylbenzylidene)-1,2-dihydro-2-imino-3-naphthoate*, m. p. 215° (Found: C, 67·8; H, 5·6; N, 6·1. $C_{27}H_{26}N_2O_6$ requires C, 68·3; H, 5·5; N, 5·9%).

The solid (94 mg.) was refluxed in methanolic sodium hydroxide during 6 hr.; the mixture afforded an acid, m. p. 166—167°, in pale yellow needles (53 mg.) (from aqueous acetic acid) which decomposed at *ca.* 150° under a vacuum to an orange gum. A different sample of lower purity was passed in aqueous acetic acid through a column of alumina to give (from aqueous acetic acid) an acid, m. p. 165—167°, orange-yellow needles which were dried at room temperature (Found: C, 64·7; H, 4·8; N, 5·3. Calc. for $C_{19}H_{13}NO_5,H_2O$: C, 64·6; H, 4·3; N, 4·0. Calc. for $C_{19}H_{12}N_2O_3,2H_2O$: C, 64·8; H, 4·6; N, 7·95%).

Reductive Acetylation of Ethyl 3-Amino-4-(α-ethoxycarbonylbenzylidene)-1,4-dihydro-2-naphthoate.—A mixture of the amine (1·03 g.), zinc dust (1·0 g.), and acetic anhydride (30 ml.) was refluxed for 15 hr. with occasional additions of further amounts of zinc. The supernatant liquid was filtered and diluted with water, giving a solid (1·2 g.), which (1 g.) was chromatographed on alumina from which benzene eluted the *acetyl derivative* (0·82 g.), m. p. 211—212° (from ethanol) [Found: C, 66·7, 67·2; H, 5·6, 5·6; N, 5·35, 5·2; O, 22·2; Ac, 18·3 (Wenzel's H_2SO_4), 22·1 (methanolic NaOH, 6 hr.); OEt, 16·1; active H, 0·08 (at 95°). Found, for a different sample: C, 67·0; H, 5·6; N, 5·5; O, 22·3. $C_{29}H_{30}N_2O_7$ requires C, 67·2; H, 5·8; N, 5·4; O, 21·6; 3Ac, 24·8; 2EtO, 17·4; H, 0·2. $C_{31}H_{32}N_2O_8$ requires C, 66·4; H, 5·75; N, 5·0; O, 22·8; 4Ac, 30·7; 2EtO, 16·1%]. Repetition of this experiment was on occasion unsuccessful, particularly when acetic acid was added to the reaction mixture. The ester failed to give the iodoform test [12] and when oxidised with chromic acid in acetic acid it did not yield a crystalline product. It was recovered (m. p. and mixed m. p.) after treatment of its warm chloroform solution with bromine.

Diethyl 7,9-Dihydro-5,9-di-imino-5H-dibenzo[c,g]*carbazole-6,8-dicarboxylate* (IX).—A solution of 2,5-di-(α-cyano-α-ethoxycarbonylmethylene)-3,4-diphenyl-3-pyrroline (VIII) (2·6 g.) in sulphuric acid was set aside for 10 days, then poured on ice and sodium carbonate. The solid so obtained (2·6 g.) was extracted with hot benzene, leaving a residue (0·3 g.); the extract was chromatographed on alumina (deactivated with 1% of 10% acetic acid) from which benzene eluted a deep yellow gum which (from chloroform–ethanol) gave the *ester* in orange-red plates (112 mg.), m. p. 267—268° (Found: C, 70·5; H, 5·15; N, 9·15, 9·25; O, 14·0; OEt, 18·0. $C_{26}H_{21}N_3O_4$ requires C, 71·1; H, 4·8; N, 9·6; O, 14·6; OEt, 20·4%).

Acetylation of Ethyl 1,3-Diamino-2-naphthoate.—Ethyl 1,3-diamino-2-naphthoate,[4] acetylated at <40°, gave a *monoacetyl derivative* in pale yellow needles (from aqueous ethanol), m. p. 161—162° (Found: C, 65·8; H, 5·95; N, 10·3; Ac, 15·0. $C_{15}H_{16}N_2O_3$ requires C, 66·2; H, 5·92; N, 10·3; Ac, 15·8%), which was also obtained in small yield from a reaction at a higher temperature. This, in chloroform, with keten afforded the *triacetyl derivative*, m. p. 169—170° [Found: C, 64·3; H, 5·7; N, 8·3; O, 22·1, 22·4; OEt, 12·9; Ac, 31·5; active H (in anisole), 0. $C_{19}H_{20}N_2O_5$ requires C, 64·0; H, 5·7; N, 7·9; O, 22·45; OEt, 12·6; 3Ac, 36·2%].

[12] Vogel, " Practical Organic Chemistry," 3rd edn., Longmans, London, 1957, p. 1069.

Action of Keten on α- and β-Naphthylamine.—The amine in chloroform was saturated with keten during 1·5 hr., the solvent was evaporated, and the residue was purified from benzene, the monoacetyl compounds, m. p. 157—158° and 132—134°, being obtained.

The author thanks the Research Committee of the University of New England for a grant, and Dr. W. Zimmermann and his staff for the microanalyses.

UNIVERSITY OF NEW ENGLAND,
ARMIDALE, N.S.W., AUSTRALIA.

[*Received, October 21st,* 1960.]