Addition Reactions of Heterocyclic Compounds. Part XL.[1] Methyl Propiolate with Some Quinolines, Isoquinolines, and Phenanthridines

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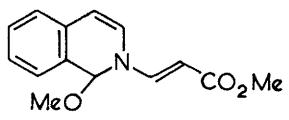
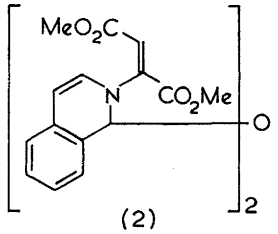
Reactions of some quinolines, isoquinolines, and phenanthridines with methyl propiolate have been investigated; the structures of the products, usually benzoindolizines, have been deduced from their u.v., n.m.r., and mass spectra.

EARLIER studies[2] of reactions between methyl propiolate and pyridines have now been extended to various benzopyridines.

The dihydroisoquinoline (1) and the benzoindolizine (3) were obtained from isoquinoline and the ester in ether, in the absence of methanol. With methanol as solvent only (1) was obtained, in much improved yield, but without solvent a violent reaction took place and chromatography of the product yielded only (3). The structure of (1) follows from its composition and spectra, and it could be formed in the same way as similar compounds from methanol, dimethyl acetylenedicarboxylate, and acridine or phenanthridine.[3] The u.v. spectrum was very similar to that[4] of the ether (2) and the n.m.r. spectrum showed as key features ester-methyl and ether-methyl resonances, a singlet corresponding to the 1-proton and an AB quartet with a high coupling constant, showing that the protons involved are *trans*.[5] In acid solution the u.v. spectrum changed to one re-



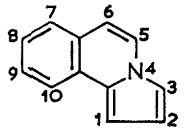
(1)



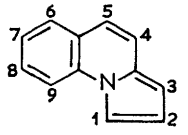
(2)

sembling that of the isoquinolinium cation formed from (2) and perchloric acid.[4] The hypsochromic shift of the longest wavelength absorption band of the cation of (2), in comparison with that from (1), is understandable, as the 2-α-ester substituent will prevent the side chain in the former case from becoming coplanar with the aromatic system. The n.m.r. spectrum of (1) in trifluoroacetic acid showed as most notable changes an enormous down-field shift for the 1-proton and the replacement of the ether-methyl resonance by that expected for methyl trifluoracetate (τ 5·91).[6] The mass spectrum showed the molecular ion and the base peak corresponding to the loss of the 1-methoxy-group and formation of the corresponding isoquinolinium cation.

The benzo[*g*]indolizine (3) has similar spectra to corresponding indolizines[2] from pyridine and 4-methylpyridine and the ester, and is probably built up in a similar way.[2] The lack of marked deshielding of protons 5 and 10 shows that the aromatic ester group must be at position 2, and the chemical shift of the single aromatic proton is consistent only with it being at position 3.



(3) 1-CH_2·CO_2Me 2-CO_2Me
(4) 1-CH_2·CO_2Me 2-CO_2Me 5-Me
(5) 1-CO_2Me 5-Me



(6) 2-CO_2Me 3-CH_2·CO_2Me
(7) 2-CO_2Me 3-CH_3·CO_2Me 7-Br
(8) 2-CO_2Me 3-CH_2·CO_2Me 7-Me
(9) 2-CO_2Me 3-CH_2·CO_2Me 9-Me
(10) 3-CO_2Me
(11) 3-CO_2Me 7-Br
(12) 3-CO_2Me 7-Me
(13) 3-CO_2Me 9-Me

The base peak in the mass spectrum corresponds to the loss of the ester group from the 1-substituent, which could give a stable cation.

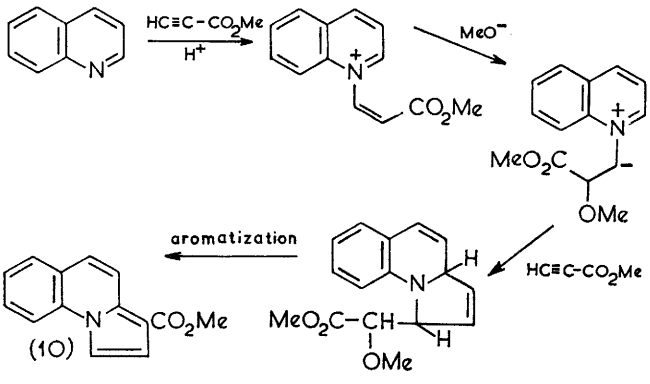
Benzopyridines with a vacant activated position adjacent to the nitrogen atom gave mixtures of two types of substituted indolizines, *viz.* (3), (4), and (6)—(9), and (5) and (10)—(13), when treated with a small excess of methyl propionate in the absence of solvent. The u.v. spectra of (3) and (4) are similar, but differ significantly from that of (5), which possesses an ester group which can participate in charged resonance forms with the ring nitrogen atom[1] to give an isoquinolinium system. Compounds (6)—(13) have similar u.v. spectra, generally resembling those of (3)—(5), which also showed no change on acidification. The positions of the substituents in the 5-membered rings can be deduced unambiguously from the deshielding effect of the aromatic ester group on adjacent and *peri*-protons. The 4- and 5-proton resonances were assigned mainly on the basis of comparisons with analogous indolizines from pyridine and the ester,[2] and also with trimethyl benzo[*e*]indolizine-1,2,3-tricarboxylate.[2] For the ester (10) the 4-proton

[1] Part XXXIX, R. M. Acheson and J. N. Bridson, *J. Chem. Soc.* (*C*), 1969, 1143.
[2] R. M. Acheson and D. A. Robinson, *J. Chem. Soc.* (*C*), 1968, 1633.
[3] R. M. Acheson, *Adv. Heterocyclic Chem.*, 1963, **1**, 125.
[4] R. M. Acheson and A. O. Plunkett, *J. Chem. Soc.*, 1964, 2676.
[5] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution N.M.R. Spectroscopy,' Pergamon, Oxford, 1966, vol. 2, p. 722.
[6] R. M. Acheson and P. J. Abbott, unpublished work.

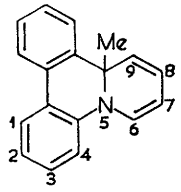
signal must be the lower-field doublet at τ 1·87, being deshielded by the 3-ester group, with the 5-proton signal appearing in the aromatic region (τ 2·0—2·85). For the diesters (6)—(9) there is no such deshielding of the 4-proton, so, on the assumption that the position of the 5-proton signal remains almost the same, the 4-proton must give the doublet which appears at higher field (τ 3·03—3·20). The mass spectra of (5) and (11) showed stable molecular ions, and the loss of a methoxy-group, which would give a resonance-stabilized cation, as the main fragmentation.

The indolizines (5) and (10)—(13) could be formed by a mechanism (Scheme) involving the participation of methanol, as is necessary for the formation of certain indolizines from pyridine and dimethyl acetylenedicarboxylate.[3]

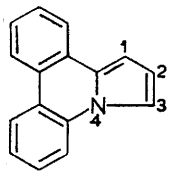
6-Methylphenanthridine and methyl propionate gave one adduct (14). Its u.v. spectrum resembled those of the corresponding tetraester (15)[7] and the 9a*H*-analogue.[8] This suggested that the two ester groups are at positions where they can interact with the nitrogen atom, for removal of ester groups in this sort of position can vastly alter the spectrum.[9] In the mass spectrometer the angular methyl group is lost to give the base peak. Although the resonance for this methyl group is 0·37 p.p.m. to lower field than that of (15)[7] it is still at too



SCHEME



(14) 7,9-di-CO_2Me
(15) 6,7,8,9-tetra-CO_2Me



(16) 1-CO_2Me
(17) 1-CO_2H
(18) 1-$CH_2{\cdot}CO_2Me$ 2-CO_2Me

high a field for it to be attached to an aromatic ring. Compound (14) could be formed by successive Michael type additions of the ester to the heterocycle, followed by cyclisation; this appears to be the first example of a cycloaddition involving methyl propiolate in which no proton shift occurs.

Phenanthridine with methyl propiolate gave (16) and (18), which correspond exactly to (10) and (6), and two other compounds, A and B. The structure of the 1-ester (16) was confirmed by hydrolysis to the acid (17) and decarboxylation to the known[10] pyrrolo-[1,2-*f*]phenanthridine. The position of the ester group is established by its deshielding effects on the 2- and 3-protons and their coupling constant, as the resonance positions of these protons in the parent ring system are known.[10] The u.v. absorption spectum of (16) shows a more complex curve than that of the 2-ester[10] or the 2,3-diester,[10] attributable to resonance interactions of the 1-ester group with the ring nitrogen atom, as for (5).

Compounds A and B were isomeric, and had distinct u.v., mass, and n.m.r. spectra, although there were strong resemblances. Both lost the fragment $CH_2{\cdot}CO_2Me$ on electron impact and the methylene groups gave AB systems in the n.m.r. spectra, suggesting attachment to asymmetric centres.

EXPERIMENTAL

The instruments and general procedures used were as described in ref. 1.

Propiolic Acid.—A scaled up literature[11] method was employed, in which prop-2-ynyl alcohol (240 g.) in a stainless steel bucket, cooled in ice–salt, was treated with the chromic acid solution, added during 5 hr., with the temperature maintained below 20°. The product (60%) had b.p. 58—64°/15 mm.

Methyl Propiolate.[12]—Concentrated sulphuric acid (7·5 g.) was added, with cooling and shaking, to propiolic acid (25 g.) and methanol (56 g.) in each of four flasks. After 5 days at room temperature distilled water (100 ml.) was added to each, with cooling. Ether (200 ml.) was then added to the combined mixture, followed by water (100 ml. or more until two phases formed). The ether layer, together with further extracts (4 × 100 ml.), was successively washed with saturated potassium hydrogen carbonate solution (2 × 250 ml.) and water (2 × 250 ml.), and dried ($MgSO_4$). Some of the ether was slowly distilled off, and the residue was fractionated with an efficient Dixon Ring (100 mesh stainless steel) column, giving the ester (89·2 g., 75%), b.p. 99—102°/765 mm.

Isoquinoline with Methyl Propiolate.—(i) Redistilled isoquinoline (0·5 g., 1 mol.) and methyl propiolate (0·58 g., 2 mol.) in sodium-dried ether (10 ml.) were left for 2 days at room temperature. Recrystallization of the resultant white and orange crystals from methanol gave *methyl 1,2-dihydro-1-methoxyisoquinolin-2-yl-trans-acrylate* (1) (200 mg., 22%) as colourless needles, m.p. 101—102·5° (Found: C, 68·5; H, 6·2; N, 6·2. $C_{14}H_{15}NO_3$ requires C, 68·6; H, 6·2; N, 5·7%), $\nu_{max.}$ 1696, 1627, 1615, 1601infl, 1568, 1494,

[7] R. M. Acheson, J. M. F. Gagan, and D. R. Harrison, *J. Chem. Soc.* (*C*), 1968, 362.
[8] R. M. Acheson and A. O. Plunkett, *J. Chem. Soc.*, 1962, 3758.
[9] R. M. Acheson and R. S. Feinberg, *J. Chem. Soc.* (*C*), 1968, 351.
[10] R. M. Acheson, A. S. Bailey, and I. A. Selby, *J. Chem. Soc.* (*C*), 1967, 2066.
[11] V. Wolf, *Chem. Ber.*, 1953, **86**, 735.
[12] D. A. Robinson, personal communication.

1439, and 1427 cm.$^{-1}$, *m/e* 245 (M^+ 15%), 214 (M — MeO, 100), and 129 (M — MeO and CH:CHCO$_2$Me, 17), *m** 187 (245 ⟶ 214).

Repetition on a five times larger scale and leaving for 5 days gave no crystals, but evaporation yielded a dark red tarry solid which was chromatographed on alumina (200 ml.). Elution of the first coloured band with light petroleum–benzene (3 : 1 v/v) gave (1) (150 mg., 3·4%), identical (m.p. and i.r. spectrum) with the analysed sample. Elution of the next (yellow) band with benzene gave *methyl 2-methoxycarbonylbenzo*[g]*indolizine-1-acetate* (3) (250 mg., 4·6%) as fine needles (from methanol), m.p. 173—174° (sublimation began at 154°) (Found: C, 68·6; H, 5·2; N, 4·9. $C_{17}H_{15}NO_4$ requires C, 68·7; H, 5·1; N, 4·7%), $\nu_{max.}$ 1734, 1702, 1640, 1602, 1552, 1517, 1505infl, 1477, 1467, 1448, 1435, and 1410 cm^{-1}, *m/e* 297 (M^+, 27·5%), 265 (M — MeOH, 22), 238 (M — CO_2Me, 100), 194 (6·5), 180 (12·5), 178 (16·5), and 170 (M — 127, 59), *m** 236 and 192 (297 ⟶ 265 and 297 ⟶ 238).

(ii) Redistilled isoquinoline (2·0 g., 1 mol.) and methyl propiolate (1·2 g., 1 mol.) were left in methanol (20 ml.) at room temperature for 3 days. Evaporation and trituration of the orange oil with petroleum gave (1) (2·0 g., 65%), identical (m.p. and i.r. spectrum) with the analysed sample.

(iii) Isoquinoline (1·0 g.) and methyl propiolate (1·0 g.) were mixed together in the absence of solvent. Within 30 sec. a very violent reaction occurred, and the resultant brown tar was chromatographed on alumina (60 ml.). Elution with benzene gave (3) (450 mg., 22·5%), identical (m.p. and i.r. spectrum) with the analysed sample.

3-Methylisoquinoline with Methyl Propiolate.—3-Methylisoquinoline (1·0 g.) and methyl propiolate (1·5 g.) were heated under reflux for 2 hr. The excess of methyl propiolate was removed by extracting the tar with boiling light petroleum (100 ml.), and the resultant tarry brown solid was chromatographed on alumina (50 ml.). Elution with light petroleum–benzene (9 : 1 v/v) gave *methyl 5-methylbenzo*[e]*indolizine-1-carboxylate* (5) (300 mg., 16·5%) as colourless rods (from methanol), m.p. 104—105° (Found: C, 75·4; H, 5·6; N, 6·0. $C_{15}H_{13}NO_2$ requires C, 75·4; H, 5·4; N, 5·9%), $\nu_{max.}$ 1691, 1655infl, 1520, 1508infl, and 1437infl cm.$^{-1}$, *m/e* 239 (M^+, 82·5%), 224 (M — Me, 3·5), 208 (M — MeO, 100), 181 (M — CO_2·CH_2, 19·5), and 152 (17); *m** 181, 156, and 103 (239 ⟶ 208, 208 ⟶ 181, and 224 ⟶ 152).

Elution of the second (yellow) band with light petroleum–benzene (3 : 1 v/v) gave *methyl 2-methoxycarbonyl-5-methylbenzo*[e]*indolizine-1-acetate* (4) (500 mg., 23%) as pale yellow parallelipipeds (from methanol), m.p. 169—170° (Found: C, 69·5; H, 5·5; N, 4·4. $C_{18}H_{17}NO_4$ requires C, 69·5; H, 5·5; N, 4·5%), $\nu_{max.}$ 1739, 1704, 1653, 1603, 1542, 1512, 1467, 1433, and 1406 cm.$^{-1}$, *m/e* (pressure uncontrollable) 311 (M^+, 21), 279 (M — MeOH, 54), 252 (M — CO_2Me, 100), 236 (7·5), 222 (92), and 208 (36), *m** 250, 228, and 196 (311 ⟶ 279, 279 ⟶ 252, and 252 ⟶ 222).

Quinoline with Methyl Propiolate.—(i) Quinoline (1·5 g.) and methyl propiolate (2·0 g.) were heated to 60° for 18 hr., and the resultant tarry brown solid was extracted with boiling light petroleum (100 ml.) and chromatographed on alumina (120 ml.). Elution with light petroleum–ether (8 : 1 v/v) gave *methyl benzo*[e]*indolizine-3-carboxylate* (10) (250 mg., 8·8%) as needles (from methanol), m.p. 135—136·5° (Found: C, 74·7; H, 5·0; N, 6·0. $C_{14}H_{11}NO_2$ requires C, 74·7; H, 4·9; N, 6·2%), $\nu_{max.}$ 1686, 1619, 1610, 1577, 1546, 1485, 1475infl, 1450, and 1421 cm.$^{-1}$.

Elution of the next (orange) band with light petroleum–ether (3 : 1 v/v) gave *methyl 2-methoxycarbonylbenzo*[e]*indolizine-3-acetate* (6) (400 mg., 11%) as pale yellow needles (from methanol), m.p. 137—138·5° (Found: C, 68·8; H, 5·1. $C_{17}H_{15}NO_4$ requires C, 68·7; H, 5·1%), $\nu_{max.}$ 1730, 1693, 1560, 1509, 1468infl, 1442infl, and 1407 cm.$^{-1}$. Further elution gave only tar.

(ii) The benzoindolizine (6) was similarly obtained (10%) from refluxing quinoline (2·85 g.) and methyl propiolate (3·26 g.) in sodium-dried ether (60 ml.) (40 hr.).

6-Bromoquinoline with Methyl Propiolate.—6-Bromoquinoline (3·75 g.) and methyl propiolate (3·0 g.) were left at room temperature for 18 hr. and the resultant brown oil was extracted with boiling light petroleum (200 ml.) and chromatographed on alumina (250 ml.). Elution of the first (pale yellow) band with light petroleum–benzene (4 : 1 v/v) gave *methyl 7-bromobenzo*[e]*indolizine-3-carboxylate* (11) (450 mg., 7·7%) as needles (from light petroleum containing a little chloroform), m.p. 179·5—181° (sublimation began at 150°) (Found: C, 55·2; H, 3·7; Br, 26·4. $C_{14}H_{10}BrNO_2$ requires C, 55·2; H, 3·3; Br, 26·4%), $\nu_{max.}$ 1690, 1620, 1612, 1572, 1543, 1488, 1432infl, and 1404 cm.$^{-1}$, *m/e* 305 (98%) and 303 (100) (M^+), 274 (98) and 272 (100) (M — OMe), 246 (16·8) and 244 (18), 193 (17), 165 (24), and 164 (19·5), *m** 246 and 244, and 221 and 219 (305 ⟶ 274 and 303 ⟶ 272, and 274 ⟶ 246 and 272 ⟶ 244).

Elution of the next (yellow) band with benzene and then with benzene–ethyl acetate (4 : 1 v/v) gave *methyl 7-bromo-2-methoxycarbonylbenzo*[e]*indolizine-3-acetate* (7) (420 mg., 6·2%) as yellow plates (from methanol), m.p. 178·5—181° (Found: C, 54·4; H, 3·9. $C_{17}H_{14}BrNO_4$ requires C, 54·4; H, 3·7%), $\nu_{max.}$ 1742, 1697, 1560, 1551, 1507, 1490, 1482infl, 1446, 1432, and 1411 cm.$^{-1}$.

Hydrogenation of Methyl 7-Bromo-2-methoxycarbonylbenzo[e]*indolizine-3-acetate.*—The indolizine (7) (100 mg.) in methanol (200 ml.) was shaken with 5% palladium–charcoal (75 mg.) for 7 hr. under hydrogen (3 atmos.), giving (6) (30 mg., 50%) as almost colourless needles (from light petroleum containing a little chloroform), m.p. 135—139°, identical (i.r., u.v., and n.m.r. spectra) with the analysed sample.

6-Methylquinoline with Methyl Propiolate.—6-Methylquinoline (1·5 g.) and methyl propiolate (2·0 g.) were heated to 105° under reflux for 6 hr. The resultant brown tar was extracted with boiling light petroleum (200 ml.) to remove the excess of methyl propiolate and then chromatographed on alumina (150 ml.). Elution of the first (colourless) band with light petroleum–ether (9 : 1 v/v) gave *methyl 7-methylbenzo*[e]*indolizine-3-carboxylate* (12) (600 mg., 23%) as parallelipipeds (from methanol), m.p. 136—137·5° (Found: C, 75·2; H, 5·3; N, 6·0. $C_{15}H_{13}NO_2$ requires C, 75·4; H, 5·4; N, 5·9%), $\nu_{max.}$ 1680, 1640, 1616, 1584, 1565, 1539, 1487, 1449, 1430infl, and 1408 cm.$^{-1}$.

Elution of the next (pale yellow) band with a 7 : 1 solvent mixture gave traces of an uncrystallisable orange oil. Elution of the next (orange) band with a 3 : 1 mixture gave *methyl 2-methoxycarbonyl-7-methylbenzo*[e]*indolizine-3-acetate* (8) (300 mg., 9·2%) as needles (from methanol), m.p. 146—147° (Found: C, 69·1; H, 5·2; N, 4·6. $C_{18}H_{17}NO_4$ requires C, 69·4; H, 5·5; N, 4·5%), $\nu_{max.}$ 1732, 1713, 1620, 1567, 1506, 1492, 1445, 1419, and 1401 cm.$^{-1}$.

8-Methylquinoline with Methyl Propiolate.—8-Methylquinoline (3·0 g.) and methyl propiolate (4·0 g.) were heated at 105° for 60 hr. Excess of methyl propiolate was removed

by boiling with light petroleum (150 ml.) and the insoluble dark brown tar was chromatographed on alumina (50 ml.). Elution of the first (yellow) band with light petroleum–ether (5 : 1 v/v) gave unchanged 8-methylquinoline (2·0 g.). Elution of the next (yellow) band with the same solvent gave *methyl* 9-*methylbenzo*[e]*indolizine*-3-*carboxylate* (13) (250 mg., 15%) as very fine needles (from methanol and then hexane), m.p. 114—115° (Found: C, 75·5; H, 5·5; N, 5·9. $C_{15}H_{13}NO_2$ requires C, 75·4; H, 5·4; N, 5·9%), $\nu_{max.}$ 1685, 1620, 1598, 1550, 1490, 1467, 1450, 1429, and 1415 cm.$^{-1}$.

Elution of the next (red) band with a 3 : 1 solvent mixture gave *methyl* 2-*methoxycarbonyl*-9-*methylbenzo*[e]*indolizine*-3-*acetate* (9) (70 mg., 8%) as rods (from methanol), m.p. 159—160° (Found: C, 69·1; H, 5·4; N, 4·7. $C_{18}H_{17}NO_4$ requires C, 69·5; H, 5·5; N, 4·5%), $\nu_{max.}$ 1741, 1712, 1570, 1510, 1477infl, 1465infl, 1432, 1420, and 1410 cm.$^{-1}$.

6-*Methylphenanthridine with Methyl Propiolate*.—6-Methylphenanthridine (1·5 g., 1 mol.) was heated with methyl propiolate (2·9 g., 4 mol.) at 105° for 65 hr. Excess of methyl propiolate was removed by boiling with light petroleum (150 ml.) and the insoluble dark brown solid was chromatographed on alumina (150 ml.). Elution of the first (yellow) band with light petroleum–ether (6 : 1 v/v) gave *dimethyl* 9a-*methyl*-9aH-*pyrido*[1,2-f]-*phenanthridine*-7,9-*dicarboxylate* (14) (520 mg., 15%) as yellow prisms (from methanol), m.p. 195—196° (Found: C, 73·2; H, 5·5; N, 3·9. $C_{22}H_{19}NO_4$ requires C, 73·2; H, 5·3; N, 3·9%), $\nu_{max.}$ 1701, 1693, 1592, 1568, 1543, 1500, 1488infl, 1452, 1438, and 1420 cm.$^{-1}$, *m/e* 361 (M^+, 55%), 346 (M — Me, 100), 330 (M — OMe, 11·5), 318 (56), 302 (M — CO_2Me, 17), 288 (22), and 272 (15), *m** 332, 291, and 261 (361 ⟶ 346, 346 ⟶ 318, and 318 ⟶ 288). Further elution of the column gave tars.

Phenanthridine with Methyl Propiolate.—Phenanthridine (7·0 g.) and methyl propiolate (9·0 g.) were heated to 105° for 24 hr. Removal of the excess of propiolate by boiling with light petroleum (250 ml.) left a dark brown tarry solid, which was chromatographed on alumina (500 ml.). Elution with light petroleum–ether (5 : 1 v/v) gave *methyl pyrrolo*[1,2-f]*phenanthridine*-1-*carboxylate* (16) (2·9 g., 27·5%) as rods (from methanol), m.p. 137—138° (Found: C, 78·4; H, 4·8; N, 5·1. $C_{18}H_{13}NO_2$ requires C, 78·6; H, 4·7; N, 5·1%), $\nu_{max.}$ 1690, 1608, 1596, 1534, 1509, and 1446 cm.$^{-1}$, *m/e* 275 (M^+ 99%), 244 (M — OMe, 100), 217 (M — CO_2CH_2, 21), 216 (M — CO_2Me, 23), 215 (24), and 189 (12), *m** 216 and 192 [275 ⟶ 244 and 244 ⟶ 216 (loss of CO)].

Elution of the next pale yellow band with a 3 : 1 solvent mixture gave *methyl* 2-*methoxycarbonylpyrrolo*[1,2-f]*phenanthridine*-1-*acetate* (18) (2·2 g., 17%) as rods (from methanol), m.p. 167·5—169° (Found: C, 72·4; H, 4·9; N, 3·9. $C_{21}H_{17}NO_4$ requires C, 72·7; H, 4·9; N, 4·0%), $\nu_{max.}$ 1726, 1708, 1595, 1546, 1519, 1501, 1484, 1444, and 1431 cm.$^{-1}$, *m/e* 347 (M^+, 26%), 315 (M — MeOH, 30·5), 288 (M — CO_2Me, 100) 272 (7·5), 258 (5·2), 244 (7·5), 230 (20), 229 (12), 228 (34), and 216 (4·5), *m** 286 (347 ⟶ 315).

Elution of the next yellow band with a 5 : 2 solvent mixture gave a mixture of orange and yellow solids (0·8 g.). Separation of this on a thin-layer plate (1 m.; 1 mm. silica gel layer) in toluene–ethyl acetate (4 : 1 v/v) gave two major components. Extraction of both bands gave yellow solids, which, from methanol, gave more of (18) (360 mg.). Evaporation of the mother liquors and recrystallisation (methanol) three times gave an intense yellow solid, m.p. 149—159°. Further purification by t.l.c. gave compound A (120 mg., 0·7%) as yellow needles, m.p. 158—160° (Found: C, 68·3; H, 5·0; N, 3·5. $C_{24}H_{21}NO_6$ requires C, 68·7; H, 5·0; N, 3·3), $\nu_{max.}$ 1736, 1700, 1676, 1627, 1505, 1478, 1433, 1405 cm.$^{-1}$, *m/e* 419 (M^+ 40·5%), 404 (29·5), 388

TABLE 1

N.m.r. spectra (100 MHz; τ values; J in Hz) for solutions in deuteriochloroform with tetramethylsilane as internal standard

	Proton resonances	Ester resonances
(1)	ArH (4H,m) 2·06—2·95; α-H(d) 2·40; β-H(d) 4·53; 1-H 3·93; 3-H(d) 3·40; 4-H(d) 4·08; 1-OMe 6·99; $J_{\alpha,\beta}$ 14·5; $J_{3,4}$ 7·5	6·27
(1) [a]	ArH (7H,m) 1·10—2·0; β-H(d) 2·86; 1-H 0·17; $J_{\alpha,\beta}$ 14·0; CF_3CO_2Me 5·92	5·90
(3)	ArH (3H,m) 2·35—2·80; 1-CH_2 5·49; 3-H 2·30; 5-H(d) 2·49; 6-H(d) 3·33; 10-H(q) [b] 1·99; $J_{5,6}$ 9·5; $J_{9,10}$ 8·2; $J_{8,10}$ 1·1	6·18, 6·31
(4)	ArH (3H,m) 2·40—2·80; 1-CH_2 5·42; 3-H 2·22; 5-Me 7·53; 6-H 3·38; 10-H(q) 1·94; $J_{9,10}$ 7·7; $J_{8,10}$ 1·3	6·12, 6·29
(5)	ArH (4H,m) 2·30—2·90; 2-H(d)2·83; 3-H(d) 2·71; 5-Me 7·49; 6-H 3·24; 10-H 0·18; [c] $J_{2,3}$ 3·1	6·07
6) [d]	ArH (3H,m) 2·30—2·90; 1-H 1·69; 3-CH_2 5·96; 4-H(d) 3·06; 5-H(d) 2·80; 9-H(q) 2·10; $J_{4,5}$ 9·6; $J_{8,9}$ 8·3; $J_{7,9}$ 1·1	6·13, 6·30
(7) [d,e]	1-H 1·77; 3-CH_2 5·98; 4-H(d) 3·20; 5-H(d) 2·80; 6-H(d) 2·35; 8-H(q) 2·52; 9-H(d) 2·37; $J_{4,5}$ 9·4; $J_{6,8}$ 1·8; $J_{8,9}$ 8·6	6·14, 6·30
(8) [d]	1-H 1·70; 3-CH_2 5·94; 4-H(d) 3·08; 5-H(d) 2·81; 6-H 2·75; [f] 7-Me 7·56; 8-H(m) 2·64; 9-H(d) 2·28; $J_{4,5}$ 9·7; $J_{8,9}$ 8·6	6·12, 6·29
(9) [d]	ArH (4H,m) 2·46—2·89; 1-H 1·27; 3-CH_2 5·93; 4-H(d) 3·03; 9-Me 7·04; $J_{4,5}$ 9·4	6·11, 6·29
(10) [d]	ArH (5H,m) 2·0—2·85; 1-H(d) 2·26; 2-H(d) 2·79; 4-H(d) 1·87; $J_{1,2}$ 2·9; $J_{4,5}$ 9·2	6·08
(11) [d]	1-H(d) 2·34; 2-H(d) 2·81; 4-H(d) 1·88; 5-H(d) 2·86; 6-H(d) 2·20; 8-H(q) 2·43; 9-H(d) 2·28; $J_{1,2}$ 3·1; $J_{4,5}$ 9·3; $J_{6,8}$ 2·0; $J_{8,9}$ 8·2	6·09
(12) [d]	1-H(d) 2·33; 2-H(d) 2·83; 4-H(d) 1·92; 5-H(d) 2·79; 6-H(d) 2·55; 7-Me 7·56; 8-H(q) 2·68; 9-H(d) 2·29; $J_{1,2}$ 2·9; $J_{4,5}$ 9·8; $J_{6,8}$ 1·0; $J_{8,9}$ 8·7	6·10
(13) [d]	ArH (3H,m) 2·34—2·88; 1-H(d) 1·79; 2-H(d) 2·83; 4-H(d) 1·80; 5-H(d) 2·79; 9-Me 7·05; $J_{1,2}$ 3·1; $J_{4,5}$ 9·4	6·08
(14)	ArH (5H,m) 2·52—2·91; 1- and 13-H(m) 2·20—2·37; 6-H 2·10; 8-H 2·68; 9a-Me 8·07; 10-H(?)(m) 2·08	6·23, 6·27
(16)	ArH (5H,m) 1·90—2·65; 3-H(d) 2·16; 2-H(d) 2·59; 12-H(m) 0·20; 8- and 9-H(m) 1·40—1·70; $J_{2,3}$ 3·1	6·06
(17) [g]	ArH (4H,m) 2·2—2·6; 2-H(d) 2·77; 3-H(d) 1·68; 5-H(?)(m) 1·65; 9- and 10-H(m) 1·25—1·55; 12-H(m) 0·20; $J_{2,3}$ 3·0	
(18)	ArH (6H,m) 1·99—2·84; 1-CH_2 5·51; 3-H 1·76; 7- and 8-H(m) 1·78—1·94	6·12, 6·27
A	ArH (6H,m) 2·4—2·9; ArH (2H,m) 2·0—2·3; singlets 1·98 (1H) and 4·23 (1H); CH_2 5·95(d) and 6·50(d), J *ca.* 17	6·18, 6·30, 6·42
B	ArH (6H,m), 2·50—2·90; ArH (2H,m) 2·05—2·40; singlets 2·35 (1H) and 4·08 (1H); CH_2 5·47(d) and 5·70(d), J 17	6·24, 6·36, 6·41

[a] In trifluoroacetic acid. [b] Could also be 7-H. [c] Doublet with further splitting. [d] The assignments for the 4-, 5-, 6-, and 9-protons were deduced from comparisons of the spectra for compounds (6)—(13). [e] The aromatic proton spectrum, calculated by use of the parameters given, in the usual way,[7] matched the observed spectrum exactly in intensities and to ±0·25 Hz in all line positions. [f] Broadened singlet. [g] In Me_2SO.

(14·5), 372 (12), 360 (12·5), 346 (100), 328 (10), and 300 (9·5), *m** 390, 357, 329, 309, and 286 [419 ⟶ 404 (*M* − Me), 404 ⟶ 388, 419 ⟶ 372, 388 ⟶ 346, and 419 ⟶ 346 (*M* − CH_2·CO_2Me)].

TABLE 2

U.v. spectra

$\lambda_{max.}$ (mμ); $10^{-4}\varepsilon$ in parentheses for methanolic solutions

(1)	209 (2·07), 240 (1·41), 302infl (1·46), 334 (3·19)
(1)*	216 (1·90), 252 (3·78), 305 (1·41), 357 (0·56)
(3)	216 (2·48), 257infl (4·78), 264 (6·73), 298 (0·47), 311 (0·50), 324 (0·50), 340infl (0·27)
(4)	219 (2·64), 258infl (4·53), 366 (6·77), 276infl (2·99), 300infl (0·50), 312 (0·57), 325 (0·54), 342 (0·36), 358infl (0·18)
(5)	218 (3·06), 243 (1·36), 266 (3·01), 275 (4·92), 313infl (0·82), 323 (1·02), 337 (0·99), 353 (0·85)
(6)	209 (2·60), 223 (2·68), 239infl (3·05), 247 (3·63), 257infl (3·07), 264infl (2·71), 271infl (1·93), 282 (1·06), 339infl (0·84), 348 (0·89), 364infl (0·59)
(7)	210 (3·19), 232 (2·77), 251 (4·05), 261infl (3·69), 269infl (3·38), 278infl (1·98), 290 (0·97), 346infl (0·85), 359 (0·97), 373infl (0·70)
(8)	213 (3·08), 231 (2·96), 241infl (2·90), 251 (4·74), 260infl (3·77), 269infl (3·23), 277infl (2·49), 288 (1·31), 341infl (1·0), 352 (1·13), 366infl (0·76)
(9)	212 (2·99), 234 (3·39), 254 (4·52), 262infl (4·29), 283infl (1·03), 339 (1·09), 345infl (1·06), 366 (0·75)
(10)	223 (3·38), 299infl (2·58), 245infl (1·58), 252 (2·04), 263 (1·58), 271 (1·67), 279infl (1·09), 323infl (0·84), 339infl (1·35), 351 (1·80), 369 (1·29)
(11)	211infl (2·52), 223 (3·43), 232infl (2·76), 250infl (2·33), 257 (3·03), 273 (2·01), 279infl (1·69), 343infl (1·26), 357 (1·69), 375 (1·23)
(12)	209infl (2·37), 223 (4·13), 232infl (2·52), 247infl (1·86), 254 (2·37), 266 (1·86), 272 (1·94), 280infl (1·43), 329infl (1·09), 341infl (1·45), 354 (1·99), 371 (1·50)
(13)	209infl (1·86), 225 (3·82), 247infl (1·72), 255 (2·0), 266 (1·93), 283infl (0·93), 335infl (1·50), 347 (2·0), 364 (1·54)
(14)	211 (3·30), 248infl (1·95), 253 (2·0), 261infl (1·90), 300 (1·97), 404 (1·78)
(16)	209 (2·68), 233 (3·68), 242 (4·36), 252infl (2·72), 275 (2·52), 282infl (2·28), 290 (1·68), 304 (1·80), 320infl (1·28), 333 (1·72), 348 (1·56)
(17)	209 (2·74), 232 (2·99), 242 (3·19), 253infl (2·26), 264 (2·06), 275 (1·98), 287 (1·83), 306 (1·35), 331 (0·99), 340 (0·93)
(18)	209 (1·93), 214 (1·93), 243 (3·32), 259infl (5·51), 265 (6·80), 276infl (2·46), 285 (1·66), 312 (0·80), 331infl (0·54)
A	211 (3·60), 253 (3·04), 269infl (2·44), 286infl (1·79), 414 (0·78)
B	211 (2·72), 260 (2·93), 287infl (1·71), 323infl (0·79), 406 (0·69), 441infl (0·54)

* After acidification.

Elution of the next deep yellow band with a 3 : 2 solvent mixture gave a mixture of white, yellow, and brown solids which, from methanol gave more of (18) (500 mg.). Evaporation of the mother liquors and separation of the resultant yellow solid (600 mg.) on a t.l.c. plate (1 m.) in toluene–ethyl acetate (4 : 1 v/v), gave six bands, all of which were extracted as before. Only the very intense yellow band, with the fourth highest R_F value, gave a significant amount of solid, which, from methanol, gave compound B (260 mg., 1·5%), as yellow, distorted parallelipipeds (from methanol), m.p. 186—189° (variable) (Found: C, 68·9; H, 5·1; N, 3·3. $C_{24}H_{21}NO_6$ requires C, 68·7; H, 5·0; N, 3·3%), $\nu_{max.}$ 1735, 1703, 1677, 1623, 1592, 1581, 1559, 1526, 1485, 1476, 1429, and 1403 cm.$^{-1}$, *m/e* (175°) 419 (M^+ 38%), 404 (*M* − Me, 19), 388 (*M* − OMe, 24), 386 (11), 360 (*M* − CO_2Me, 73), 346 (*M* − CH_2·CO_2Me, 100), 344 (25), 330 (44), and 328 (6·8), *m** 356, 342, and 286 (404 ⟶ 388, 404 ⟶ 372, and 419 ⟶ 346), *m/e* (190°) 419 (M^+, 0·5%), 376 (1·0), 360 (1·8), 346 (4·8), 344 (5·7), 330 (100), 315 (65), 283 (5·6), and 256 (12·5), *m** 315, 301, and 254 (346 ⟶ 330, 330 ⟶ 315, and 346 ⟶ 298).

Hydrolysis of Methyl Pyrrolo[1,2-f]*phenanthridine-1-carboxylate*.—The ester (16) (1·0 g.) was dissolved in a solution of sodium hydroxide (10 g.) in methanol (60 ml.) and water (20 ml.) and refluxed for 5 hr. Acidification with dilute hydrochloric acid, partial evaporation, and extraction with chloroform (3 × 25 ml.) gave *pyrrolo*[1,2-f]*phthanthridine-1-carboxylic acid* (17) (800 mg., 84%) as needles (from benzene), m.p. 195—196° (decomp.) (Found: C, 77·9; H, 4·5; N, 5·5. $C_{17}H_{11}NO_2$ requires C, 78·2; H, 4·2; N, 5·4%), $\nu_{max.}$ 3250—2700, 1660, 1607, 1594, 1580, 1560, 1530, 1512, 1474, 1447, and 1400 cm.$^{-1}$.

Decarboxylation of Pyrrolo[1,2-f]*phenanthridine-1-carboxylic Acid*.—The acid (17) (130 mg.) and soda lime (1·0 g.) were ground together to ensure intimate mixing, and then heated to red heat for 10 min. in a Pyrex tube, fitted with a vertical air condenser. Extraction of the condenser and residue with chloroform (3 × 25 ml.), filtration, and evaporation gave pyrrolo[1,2-*f*]phenanthridine (60 mg., 63%) as needles, m.p. 148—151° (lit.,[7] 150·5—151°; sublimation began at 125°), identical (i.r., u.v., and n.m.r., spectra) with the literature [7] specimen.

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