Addition Reactions of Heterocyclic Compounds. Part LIV.[1,2] Rotational Isomerism of 6-Aralkyl-5-oxidovinylphenanthridiniums: an Investigation by Variable Temperature Nuclear Magnetic Resonance Spectroscopy

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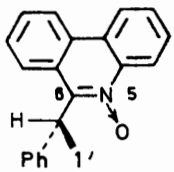
6-Aralkyl-5-oxidovinylphenanthridiniums have been synthesised and shown to exhibit rotational isomerism by variable temperature nuclear magnetic resonance spectroscopy. The oxidovinyl compounds obtained from 6-benzylphenanthridine 5-oxide and methyl propiolate or dimethyl acetylenedicarboxylate have been converted into 1-phenylpyrrolo[1,2-*f*]phenanthridines.

Two types of isomerism, one geometrical and one rotational, have been observed among 6-aryl-5-oxidovinylphenanthridiniums.[3,4] For compounds such as 6-*o*-tolyl-5-(1-methoxycarbonyl-2-oxidovinyl)phenanthridinium the vinyl group can give rise to *cis–trans* isomers; also, because the rotation of the 5- and 6-substituents about the bonds joining them to the phenanthridine system is impossible for steric reasons, stable ' rotamers ', differing in the *cis* or *trans* arrangement of the *o*-tolyl methyl group and the ester group, exist. We now report a variation of the rotational type which has been observed among the 6-aralkyl analogues of these compounds. 6-Alkyl-5-oxidovinylphenanthridiniums have been prepared previously;[5] their n.m.r. spectra did not show any complexities attributable to hindered molecular motion. The compounds used in the present study were prepared from phenanthridine 5-oxides with the appropriate acetylenic ester by the method previously described;[3-5] their u.v., i.r., and mass spectra were similar to those of the known analogues.

The n.m.r. spectrum of one of the oxides used (1) showed a remarkable downfield shift (1·21 p.p.m.) of the methine proton resonance compared with that of the unoxidised phenanthridine; this is largely due to the preferred conformation shown where the *N*-oxide group forces the methine hydrogen atom into the deshielding zone of the phenanthridine benzene ring. For similar reasons the signal for the methine proton of (2) appears in the aromatic region.

6-Benzyl-5-(1,2-dimethoxycarbonyl-2-oxidovinyl)-phenanthridinium (3) gave an n.m.r. spectrum which showed the expected signals except that the benzylic



(1) 1'-Me
(2) 1'-Ph

methylene protons appeared as an AB quartet. It has recently been concluded [6] that such a quartet is a positive indication of molecular chirality. Whether such chirality is due to intrinsic asymmetry,[7] or to the existence of a preferred conformation whose lifetime is long compared with the n.m.r. transition time, can in general be discovered by variable temperature n.m.r. studies since magnetic non-equivalence due to intrinsic asymmetry is temperature-independent whereas magnetic non-equivalence due to a preferred conformation disappears when conformational interconversion becomes fast on the n.m.r. time-scale.

At 41° the n.m.r. spectrum of (3) (Table 2; $CDCl_3$; 100 MHz) showed a broad signal without fine structure for

[1] Part LIII, R. M. Acheson and M. S. Verlander, *J.C.S. Perkin I*, 1973, 2348.
[2] Presented in part at the International Symposium on Nuclear Magnetic Resonance Spectroscopy, Birmingham, July, 1969.
[3] R. M. Acheson and I. A. Selby, *Chem. Comm.*, 1970, 62.
[4] R. M. Acheson and I. A. Selby, *J. Chem. Soc.* (*C*), 1971, 691.
[5] R. M. Acheson, A. S. Bailey, and I. A. Selby, *J. Chem. Soc.* (*C*), 1967, 2066.
[6] R. E. Lyle and J. J. Thomas, *Tetrahedron Letters*, 1969, 897.
[7] M. van Gorkom and G. E. Hall, *Quart. Rev.*, 1968, **22**, 26.

the methylene protons; at 100° this signal was sharp. These changes were reversed on cooling and occurred in exactly the same way after filtration of the solution through calcium oxide to remove possible traces of deuterium chloride which would speed up any *cis–trans* equilibration of the 5-substituent.[3,4] It is concluded that at room temperature preferred chiral conformations exist which are enantiomeric (3a and b) and that at elevated temperatures these interconvert rapidly by partial rotation of the 5- and 6-substituents about the bonds joining them to the phenanthridine ring. This process exchanges the environments of the methylene protons and thus renders them magnetically equivalent.[7] In the disfavoured conformation with the benzyl phenyl ring at 90° to the plane of the phenanthridine system and over the 7-hydrogen atom, the ring is only 1·2 Å remote from that atom (measured from Dreiding models). Similar consideration of the oxidovinyl group indicates that both 5- and 6-substituents will have preferred conformations which are non-coplanar with the phenanthridine ring system. The minimum steric congestion would be expected when these substituents are oriented with their bulkiest groups on opposite sides of the phenanthridine plane as shown for (3a and b). Greater non-equivalence of the methylene protons was observed in the n.m.r. spectrum of (3) in trifluoroacetic acid; this

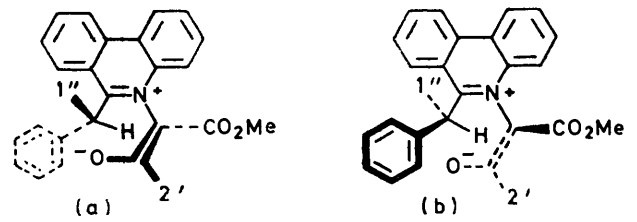
TABLE 1

^{1}H N.m.r. spectra (100 MHz; τ values; *J* in Hz) for solutions in deuteriochloroform at 34° with tetramethylsilane as internal standard

2-Diphenylacetamidobiphenyl	ArH + NH (19H, m) 2·4—3·1; 3-H (1H, d) 1·55 [a], *J* 8; methine (1H) 5·07
2-(2-Phenylpropionamido)biphenyl	ArH + NH [b] (14H, m) 2·5—3·2; 3-H (1H, d) 1·60 [a], *J* 8; methine (1H, q) 6·64, *J* 7; Me (3H, d) 8·58, *J* 7
2-Acetamidobiphenyl	ArH + NH (9H, m) 2·4—2·9; 3-H (1H, d) 1·86 [a] *J* 8; Me (3H) 8·09
2-Benzylaminobiphenyl [c]	ArH (14H, m) 2·4—3·5; CH_2 (2H) 5·70; NH not visible [d]
6-Benzylphenanthridine	ArH (13H, m) 1·4—2·9; CH_2 (2H) 5·26
6-Diphenylmethylphenanthridine	ArH (18H, m) 1·3—2·9; methine (1H) 3·52
6-(1-Phenylethyl)phenanthridine	ArH (13H, m) 1·3—2·9; methine (1H, q) 4·92, *J* 6·66; Me (3H, d) 8·07, *J* 6·66
6-Benzylphenanthridinium chloride	ArH (13H, m) 0·7—0·85, 1·15—1·5, 1·7—2·9; CH_2 (2H) 4·63; 5-H [e]
6-Benzyl-5-ethylphenanthridinium iodide	ArH (13H, m) 0·5—0·7, 1·0—1·5, 1·6—2·2, 2·3—2·8; 6-CH_2 (2H) 4·50; 5-C*H*$_3$·CH_2 (3H, t) 8·75; 5-CH_3·C*H*$_2$ (2H, q) 6·26, *J* 7
6-(1-Phenylethyl)phenanthridinium chloride	ArH (13H, m) 1·3—1·9, 2·1—2·9; methine (1H, q) 4·84, *J* 8; Me (3H, d) 8·07, *J* 8; 5-H [e]
6-Benzylphenanthridine 5-oxide	ArH (13H, m) 0·9—1·1, 1·4—1·6, 1·9—2·9; CH_2 (2H) 5·03
6-Benzoylphenanthridine 5-oxide	ArH (13H, m) 1·0—1·5, 1·7—2·65
(1) [c]	ArH (13H, m) 0·9—1·1, 1·4—1·65, 2·05—2·9; methine (1H, q) 3·71, *J* 7; Me (3H, d) 8·03, *J* 7
(2)	ArH + methine (19H, m) 1·0—1·15, 1·44—1·62, 2·08—3·0
(2) [c,g]	ArH + methine (19H, m) 0·75—2·75
(3) [f]	ArH (13H, m) 1·2—1·6, 1·8—2·4, 2·6—2·9; CH_2 (2H, ABq) 4·86, *J* 15; OMe (6H) 6·01, 6·81
(3) [g]	ArH (13H, m) 0·8—1·1, 1·3—2·0, 2·5—2·9; CH_2 (2H, ABq) 4·49, 5·16, *J* 15; OMe (6H) 5·73, 6·60
(4)	ArH (13H, m) 1·3—1·6, 1·9—3·0; vinyl H (1H) 0·23; CH_2 (2H) 3·72 [h] (13); OMe (3H) 6·40
(4) [g]	ArH (13H, m) 0·8—1·0, 1·3—2·0, 2·4—2·9; vinyl H (1H) 1·25; CH_2 (2H, ABq) 3·56, *J* 16; OMe (3H) 6·25
(4) [j]	ArH (13H, m) 1·0—1·2, 1·5—2·3, 2·6—3·0; vinyl H (1H) 1·20; CH_2 (2H) 3·70; Me (3H) 6·41
(4) [k]	Vinyl H (1H) −0·30; CH_2 (1H) 3·55 [h] (7 [i]); OMe (3H) 6·20
(5) [l]	ArH (13H, m) + methine (1H, 35%) 1·0—1·6, 1·7—2·9; methine (1H, 65%, q) 3·88, *J* 7; OMe (3H, 100%) 6·07, (3H, 68%) 6·40, (3H, 32%) 6·52; 1-Me (3H, 36%, d) 7·58, (3H, 64%, d) 7·83, *J* 7
(5) [g,l]	ArH (13H, m) + methine (1H, 50%) 0·8—1·1, 1·2—2·9; methine (1H, 50%, q) 4·35, *J* 7; OMe (3H, 100%) 5·75, (3H, 49%) 6·10, (3H, 51%) 6·20; 1′-Me (3H 49%, d) 7·50, (3H, 51%, d) 7·72, *J* 7
(5) [g,m]	ArH (13H, m) 0·8—1·2, 1·4—2·8; methine (1H, q) 4·34, *J* 7; OMe (6H) 5·75, 6·09; 1′-Me (3H, d) 7·72, *J* 7
(5) [g,n]	ArH + methine (14H, m) 0·8—1·0, 1·2—2·8; OMe (6H) 5·75, 6·17; 1′-Me (3H, d) 7·50, *J* 7
(8)	ArH (13H, m) 2·4—3·0; (1H, d) 3·19, *J* 8; CH_2 (2H, ABq) 4·62, 6·49, *J* 14; C*H*$_3$·CH_2 (3H, t) 8·92, *J* 7; CH_3·C*H*$_2$ (2H, m) 7·85
(8) [k]	CH_2 (2H, ABq) 4·44, 6·24, *J* 14; C*H*$_3$·CH_2 (3H, t) 8·87; CH_3·C*H*$_2$ (2H, m) 7·77, *J* 7
(10)	ArH (22H, m) 1·9—3·5; CH_2 (2H) 5·00; CH_3 (3H) 8·09; C*H*$_3$·CH_2 (3H, t) 8·84; CH_3·C*H*$_2$ (2H, q) 7·36, *J* 7
(11)	ArH (13H, m) 1·6—1·9, 2·2—3·0; 2-CO_2Me (3H) 6·36; 3-CO_2Me (3H) 5·96
(12)	ArH (13H, m) 1·6—1·8, 1·9—2·1, 2·1—2·3, 2·4—2·9; 2-H (1H) 2·57; 3-CO_2Me (3H) 6·06
(12) [c]	ArH (13H, m) + 2-H (1H) 1·55—3·0; 3-CO_2Me (3H) 6·06
(13) [c,o]	ArH (13H, m) 1·3—1·7, 2·2—2·9; 3-H (1H) 1·15; CO_2H [e]
(14)	ArH (13H, m) 1·65—1·9, 2·0—2·2, 2·4—3·0; 3-H (1H) 1·60; 2-CO_2Me (3H) 6·30
(15) [c]	ArH (13H, m) 1·6—1·9, 2·0—3·0; 2-H (1H, d) 3·34, *J* 2·9; 3-H (1H, d) 2·19, *J* 2·9

[a] Shows signs of further splitting. [b] Slowly exchanges with D_2O. [c] 60 MHz spectrum. [d] HOD signal appeared at τ 5·30 with D_2O. [e] Not observed. [f] Same spectrum observed in $CDCl_3$–DCl. [g] Solvent CF_3·CO_2H. [h] Broad. [i] Band-width (Hz) at half-height. [j] Solvent $CDCl_3$–PCl_3. [k] Solvent $PhNO_2$. [l] Unresolved mixture. [m] Isomer of R_F 0·4. [n] Isomer of R_F 0·25. [o] Solvent $(CD_3)_2SO$.

may result from the formation of the relatively rigid, hydrogen-bonded enol structure (6).



(3) 1″-H, 2′-CO_2Me
(4) 1″-H, 2′-H
(5) 1″-Me, 2′-CO_2Me

6-Benzyl-5-(1-methoxycarbonyl-2-oxidovinyl)phenanthridinium (4) (in $CDCl_3$) exhibited a similar phenomenon: the benzylic protons gave rise (reversibly) to an AB quartet at 5°, a broad singlet at 25°, and a sharp singlet (τ 3·72) at 90°. No changes occurred in the rest of the spectrum and it appears that (4) exhibits the same type of slow libration as (3) involving the conformations (4a and b). The sharp vinyl proton resonance at τ 0·23 was 0·68 p.p.m. to lower field of the corresponding signal of the 6-phenyl analogue of (4), presumably because in the latter case the vinyl proton is shielded by the non-coplanar phenyl group.[4] The n.m.r. spectrum of (4) in trifluoroacetic acid showed an upfield shift of the vinyl proton of *ca.* 1 p.p.m. compared with a solution in $CDCl_3$, as a result of protonation and formation of (7).[3,4] The methylene protons appeared as a distinct AB quartet.

TABLE 2

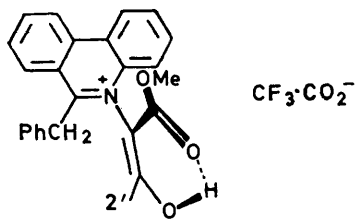
Variable temperature ^1H n.m.r. spectra

Compound	Frequency (MHz)	Solvent	Temp. (°C)	τ Values
(3)	100	$CDCl_3$	100	OMe (6H) 6·00, 6·79; CH_2 (2H) 4·85
			41	OMe (6H) 6·01, 6·80; CH_2 (2H) 4·83 [a] (4 [b])
			34	OMe (6H) 5·97, 6·81; CH_2 (2H) 4·85 ABq, J 15
(4)	60	$CDCl_3$	90	OMe (3H) 6·40; CH_2 (2H) 3·74; vinyl H (1H) 0·21
			25	OMe (3H) 6·40; CH_2 (2H) [d] (9 [b]); vinyl H (1H) 0·21
			5	OMe (3H) 6·40; CH_2 (2H) 3·69 ABq J 10; vinyl H (1H) 0·25
(8)	60	$PhNO_2$	200	NCH_2 (2H) 5·39; OCH_2 (2H) 7·80q, J 7
			160	NCH_2 (2H) 5·39 [a] (10 [b]); OCH_2 (2H) 7·80q, J 7
			120	NCH_2 (2H); [c] OCH_2 (2H) 7·80q, J 7
			100	NCH_2 (2H) 4·70 [a], 6·10 [a]; OCH_2 (2H) 7·80q, [d] J 7
			40	NCH_2 (2H) 4·45d, 6·26d, J 15; OCH_2 (2H) 7·70m

[a] Broad. Band-width (Hz) at half-height. [c] Not visible. [d] Shows signs of further splitting.

In order to confirm the view that (3) and (4) exhibited slow interconversion of enantiomeric forms, 5-(1,2-bismethoxycarbonyl-2-oxidovinyl)-6-(1-phenylethyl)phenanthridinium (5), which was expected to possess two chiral centres, was synthesised by the standard route from racemic 2-phenylpropionic acid, and had the expected u.v., i.r., and mass spectra. The n.m.r. spectra in deuteriochloroform and trifluoroacetic acid showed complex high-field regions. In the absence of stereochemical complications one would expect to observe signals for aromatic protons, methoxy-protons (2 singlets), a methine proton (quartet), and aliphatic methyl protons (doublet). In fact *two* sets of peaks were obtained in both solvents; this is the expected consequence of incorporating a second chiral centre into the molecule (3). There are considered to be four species present: two diastereoisomers each present in racemic modification (5a—d).

The diastereomeric rotamers were separated by t.l.c. and had analytical data, i.r. and u.v. spectra, and m.p.s which were mutually similar and similar to those of the unresolved mixture. Their n.m.r. spectra were different



(6) 2′-CO_2Me
(7) 2′-H

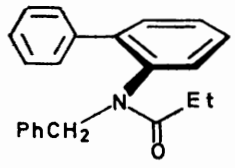
and when summed gave a spectrum identical with that of the unresolved mixture. One attempt to convert the rotameric forms into the original rotamer mixture was unsuccessful. Few cases have been reported of the isolation of racemic diastereoisomers which exist as such solely owing to hindered rotation, but these include certain steroids [8] and hydrazones.[9]

The preparation of (3) was complicated by the concomitant production of an impurity which could not itself be obtained free from the major product. It was provisionally identified as the 6-benzoyl analogue of (3) from its n.m.r. spectrum, calculated by difference, which contained signals for 13 aromatic protons and two methoxy-groups (τ 6·03 and 6·50).

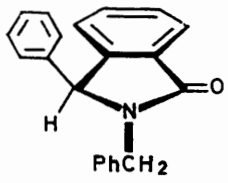
6-Benzyl-5-ethyl- and 5-benzyl-6-ethyl-phenanthridinium iodides were required as model compounds. The former was obtained by direct quaternisation of the phenanthridine and it was hoped to prepare the latter by cyclisation of the amide (8), which was obtained from 2-benzamidobiphenyl [3,4] by reduction and propionylation. Compound (8) showed an unexpectedly complex

[8] F. Kohen, R. A. Mallory, and I. Scheer, *Chem. Comm.*, 1969, 580.
[9] A. Mannschreck and U. Kolle, *Angew. Chem.*, 1969, **81**, 540.

n.m.r. spectrum ($CDCl_3$; 34°) containing an AX system for the benzylic methylene group and an ABX_3 system for the ethyl group protons. The large difference (1·87 p.p.m.) between the two signals of the AX system



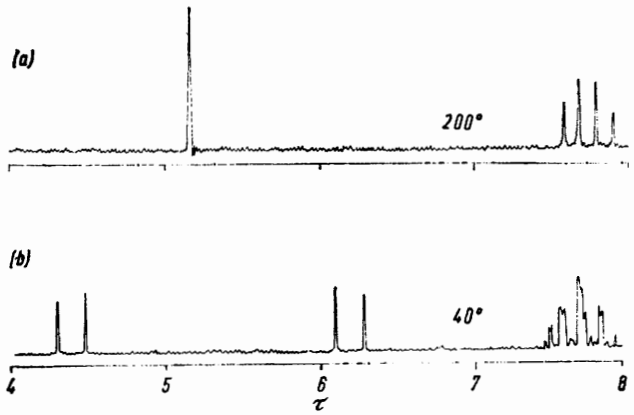
(8)



(9)

is paralleled by that found for the benzylic methylene protons of the phthalimidine (9), where the methylene group is in a similar environment.[10] The ABX_3 system was accurately simulated by our seven-spin n.m.r. program.[11] At 120° the peaks of the AX system had broadened such that no signal was detectable, but at 140° a broad peak appeared at τ 5·39 and at 200° this was a sharp singlet (see Figure). Similarly, at 120° the AB part of the ABX_3 system had simplified to a normal quartet (τ 7·80). We concluded that the complexity of the 34° spectrum is due to the existence of a preferred conformation.

Further evidence regarding the solution conformation of compounds (3), (5) (R_F 0·4), and (8) has been obtained recently [12] by examination of their n.m.r. spectra in the



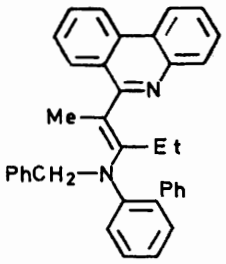
N.m.r. spectra of compound (8) at 60 MHz: (*a*) in $PhNO_2$ at 200°; (*b*) in $CDCl_3$ at 40°

presence of tris-{2,2,2-trifluoro-1-[(+)-2-oxobornan-3-yliden]ethoxy}europium(III). In each case two equal sets of signals showed the presence of equal concentrations of enantiomeric rotamers.

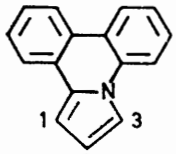
Attempts to cyclise (8) with phosphoryl chloride gave only a low yield of a product tentatively identified as (10) from its spectra.

Vacuum sublimation of the vinyloxides (3) and (4) gave the corresponding pyrrolo[1,2-*f*]phenanthridines (11) and (12). As the 1-methyl analogue of (11) [5] showed methoxy-resonances at τ 5·98 and 6·08, the higher field position (τ 6·36) of one of these resonances in the spectrum of (11) suggests that it is due to the 2-methoxycarbonyl group shielded by the non-coplanar 1-phenyl substituent. Hydrolysis of (11) or (3) gave a pyrrolo[1,2-*f*]phenanthridinemonocarboxylic acid (13), converted into the ester (14) with diazomethane, and this ester showed a high-field methoxy-resonance (τ 6·30) suggesting that the group was at position 2. The phenyl group of (16) exerts a similar shielding effect on the 3-methoxycarbonyl group,[5] but compound (12) has a normal-field ester resonance.

The cyclisation (4) ⟶ (12) confirms the earlier assignment [3-5] of the oxidovinyl structure, which was



(10)



(11) 1-Ph, 2-CO_2Me, 3-CO_2Me
(12) 1-Ph, 3-CO_2Me
(13) 1-Ph, 2-CO_2H
(14) 1-Ph, 2-CO_2Me
(15) 1-Ph
(16) 2-Ph, 3-CO_2Me
(17) 2-Ph

based on the anticipated shorter wavelength i.r. absorption band of a 1′-methoxycarbonyl group compared with that of a 2′-methoxycarbonyl group. The latter is not conjugated with the oxide function and has the normal absorption.

Decarboxylation of (13), or hydrolysis and decarboxylation of (12), gave 1-phenylpyrrolo[1,2-*f*]phenanthridine (15), identified by its spectral properties. The u.v. spectrum was typical of the class of compound and the i.r. spectrum showed no carbonyl absorptions. The mass spectrum showed the expected molecular ion peak and the n.m.r. spectrum contained only low-field resonances including an AB quartet for the 2- and 3-protons. The chemical shifts of the 2- and 3-protons of (15) and of pyrrolo[1,2-*f*]phenanthridine are very similar; this seemed surprising since the non-coplanar phenyl group might be expected to exert some influence on the 2-proton. However the 2-proton may be near the boundary of the shielding and deshielding zones and this is in agreement with Johnson–Bovey data.[13] A similar observation can be made regarding (16) and (17).[5] In (16) the 2-phenyl group is forced into a non-coplanar conformation by the 3-methoxycarbonyl group, which accordingly appears at higher field than usual. Removal of the methoxycarbonyl group gives (17) where the phenyl group is free to take up a coplanar conformation. This change in structure however only causes a shift of 0·1 p.p.m. in the resonance position of the 1-proton.

The main characteristic of the hydrolyses was the

[10] A. H. Lewin, J. Lipowitz, and T. Cohen, *Tetrahedron Letters*, 1965, 1241.
[11] C. L. Wilkins and C. E. Klopfenstein, *J. Chem. Educ.*, 1966, **43**, 10; P. C. Bell. Part II Thesis, Oxford, 1967.
[12] R. M. Acheson and I. A. Selby, *J.C.S. Chem. Comm.*, 1973, 537.
[13] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012, quoted in J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1965, p. 595.

consistent loss of the 3-methoxycarbonyl substituent from the pyrrolo[1,2-*f*]phenanthridines, or of the 1-methoxycarbonyl group from the oxidovinyl compounds. This ready decarboxylation is paralleled by the ready loss of carboxy-groups from positions 1 and 3 in indolizines [14] and position 2 in pyrroles.[15] Recent calculations of the electron densities for pyrrolo[1,2-*f*]phenanthridine [16] show a relatively high electron density at position 3 (there is a similarly high value at position 3 of indolizine[17]) and this may explain the ready decarboxylation.

EXPERIMENTAL

Quoted i.r. absorptions are usually in the range 5—7 μm. Instruments and general procedures have been described.[18] Light petroleum had b.p. 60—80° unless stated otherwise, and chromatography was carried out over deactivated alumina.

2-Amidobiphenyls were prepared by the method described,[3,4] but 2-(2-phenylpropionamido)biphenyl was distilled *in vacuo* (b.p. 193—195° at 0·07 mmHg), and 2-phenylacetamidobiphenyl [m.p. 89—91° (from ether)] and 2-diphenylacetamidobiphenyl [m.p. 152—153° (from petroleum)] were chromatographed and eluted in light petroleum and benzene respectively prior to recrystallisation.

2-Benzylaminobiphenyl was prepared by reduction of 2-benzamidobiphenyl with lithium aluminium hydride in tetrahydrofuran by a published method.[19]

Phenanthridines.—6-Benzyl-, 6-(1-phenylethyl)-, and 6-diphenylmethyl-phenanthridine were prepared from the 2-amidobiphenyls by the method described.[3,4]

6-Benzoylphenanthridine was prepared from the 5-oxide (70 mg) and phosphorus trichloride (5 ml) in dry, ethanol-free chloroform. The solution was stirred for 4 h and then evaporated to dryness *in vacuo*. The residue was dissolved in chloroform, washed with sodium hydroxide solution (2N) and water, dried, and evaporated to give the phenanthridine.

6-Benzyl-5-ethylphenanthridinium Iodide.—6-Benzylphenanthridine (2 g) and ethyl iodide (20 ml) were heated in a glass bomb at 120° for 5 h. The orange crystalline product was washed with ether.

Phenanthridine 5-Oxides.—The phenanthridines were oxidised by hydrogen peroxide as described,[3,4] but the crude products were chromatographed and eluted with benzene–ether or ether before crystallisation.

6-Benzoylphenanthridine 5-oxide was prepared by refluxing 6-benzylphenanthridine 5-oxide (2 g), selenium dioxide (1·5 g), and pyridine (25 ml) for 2 h, filtration (hot), and addition of water (50 ml) to precipitate the product.

6-Benzyl-5-(1,2-bismethoxycarbonyl-2-oxidovinyl)phenanthridinium (3).—6-Benzylphenanthridine 5-oxide (2 g) in benzene (25 ml) and dimethyl acetylenedicarboxylate (5 ml) were left for 15 h at room temperature. The yellow crystals were then collected; t.l.c. of the product on silica gel [ethanol–ether (3 : 17) as eluant] showed two yellow components at R_F 0·25 and 0·4. The n.m.r. spectrum showed two sets of signals in the methoxy-region.

The yellow precipitate was chromatographed; the fraction eluted in ethanol–ether (1 : 4) was recrystallised from chloroform–hexane (2 : 1) and rechromatographed. Elution with ethanol–ether (1 : 9) gave (3), which on t.l.c. (silica gel) [ethanol–ether (3 : 17) as eluant] showed one spot at R_F 0·4. Elution with ethanol followed by preparative t.l.c. [ethanol–ether (3 : 7)] gave bands at R_F 0·38 and 0·41. Resolution of the components was not complete and the slower moving part of the R_F 0·38 band on rechromatography gave, after recrystallisation, a product containing (n.m.r.) 40% of (3) and 60% of 6-benzoyl-5-(1,2-bismethoxycarbonyl-2-oxidovinyl)phenanthridinium.

Attempts to prepare this last compound by oxidation of (3) with selenium dioxide in pyridine, *m*-chloroperoxybenzoic acid, or peracetic acid, and from 6-benzoylphenanthridine 5-oxide with dimethyl acetylenedicarboxylate, failed.

6-Benzyl-5-(1-methoxycarbonyl-2-oxidovinyl)phenanthridinium (4).—6-Benzylphenanthridine 5-oxide (3 g) in chloroform (25 ml) and methyl propiolate (6 ml) were left for 10 days at room temperature, after which the solution was concentrated *in vacuo* and chromatographed. The product was eluted in ethanol–ether (1 : 4). T.l.c. showed only one component.

5-(1,2-Bismethoxycarbonyl-2-oxidovinyl)-6-(1-phenylethyl)-phenanthridinium (5).—6-(1-Phenylethyl)phenanthridine 5-oxide (1 g) in benzene (50 ml) and dimethyl acetylenedicarboxylate (2 ml) were left for 37 h at room temperature, after which the orange crystalline precipitate was filtered off, washed with benzene, dried *in vacuo*, and recrystallised (chloroform–light petroleum) to give a crystalline solid, m.p. 214—217°. Preparative t.l.c on silica gel [acetonitrile–chloroform (1 : 1)] gave bands at R_F 0·4 and 0·25, and these were extracted with hot acetone and chloroform. The extracts were evaporated to dryness and the products recrystallised (chloroform–light petroleum) to give yellow crystals, in each case of m.p. 214—217°. Samples of both components were heated at 120° *in vacuo* for 2 h and shown (t.l.c.) to be unchanged.

N-Benzyl-N-(biphenyl-2-yl)propionamide (8).—2-Benzylaminobiphenyl (13 g) in dry pyridine (25 ml) was treated with propionyl chloride (30 ml) in portions with stirring. The solution was stirred at 120° for 15 min, cooled, diluted three times with chloroform, and treated with an excess of 2N-hydrochloric acid. The chloroform layer was separated washed with potassium carbonate solution (20% aqueous) and water, and then dried. Evaporation left a dark oil which was chromatographed. The amide (8) (11 g) was eluted in benzene.

The ABX_3 part of the 100 MHz n.m.r. spectrum of (8) was simulated to ±0·4 Hz on any line by use of our seven-spin n.m.r. program [11] with the following input parameters: H_A 7·928; H_B 7·804; H_X 8·920; J_{AB} −16·4; $J_{AX} = J_{BX}$ = 7·4 Hz.

3-(N-Benzylbiphenyl-2-ylamino)-2-phenanthridin-6-yl)pent-2-ene (10).—*N*-Benzyl-*N*-(biphenyl-2-yl)propionamide (8) (4 g) was refluxed with phosphoryl chloride (25 ml) for 1·5 h. Evaporation *in vacuo* left an oily residue which was dissolved in benzene–chloroform (1 : 1; 50 ml); the solution was washed with aqueous sodium carbonate (20%; 50 ml) and water and evaporated to dryness and the residue was recrystallised to give (10) (0·7 g).

Dimethyl 1-Phenylpyrrolo[1,2-f]phenanthridine-2,3-dicarboxylate (11).—Compound (3) (0·5 g) was heated *in vacuo* at

[14] R. H. Wiley and L. H. Knabeschuh, *J. Org. Chem.*, 1953, **18**, 836.
[15] R. M. Acheson, ' Introduction to the Chemistry of Heterocyclic Compounds,' 2nd edn., Interscience–Wiley, New York, 1967, p. 209.
[16] V. Galasso and G. de Alti, *Tetrahedron*, 1969, **25**, 2259.
[17] Ref. 15, p. 176.
[18] R. M. Acheson, J. M. F. Gagan, and D. R. Harrison, *J. Chem. Soc.* (*C*), 1968, 362.
[19] R. B. Moffett, *Org. Synth.*, 1953, **33**, 32.

TABLE 3

U.v. spectra (ethanolic solutions; $\lambda_{max.}$ in nm.; 10^{-4} ε in parentheses)

2-Phenylacetamidobiphenyl	217 (2·56), 225 * (2·41), 250 * (0·37)
2-(2-Phenylpropionamido)biphenyl	209 (3·85), 230 * (2·01), 250 * (1·19)
2-Diphenylacetamidobiphenyl	211 (4·95), 235 * (2·04), 255 * (1·21)
2-Benzylaminobiphenyl	212 (3·41), 227 * (2·37), 255 * (0·83), 310 (0·37)
2-Benzylaminobiphenyl [a]	212 (3·25), 235 * (0·92), 254 * (0·42)
6-Benzylphenanthridine	222 (3·87), 253 (4·49), 275 (0·67), 294 (0·67), 331 (0·26), 347 (0·26)
6-Benzylphenanthridine [a]	209 (4·40), 252 (7·20), 322 (0·14), 355 (0·10), 372 * (0·10)
6-(1-Phenylethyl)phenanthridine	217 (3·39), 255 (5·11), 275 * (1·15), 300 * (0·58), 329 (0·23), 344 (0·22)
6-(1-Phenylethyl)phenanthridine [a]	211 (2·48), 255 (4·64), 275 * (1·10), 320 (0·91), 365 * (0·62)
6-(Diphenylmethyl)phenanthridine	215 (4·44), 253 (4·78), 273 * (1·26), 290 * (0·79), 330 (0·33), 345 (0·33)
6-(Diphenylmethyl)phenanthridine [a]	210 (3·58), 253 (4·31), 273 * (1·46), 325 (0·86), 365 (0·66)
6-Benzoylphenanthridine	215 (3·62), 247 (3·84), 273 * (0·98), 300 (0·91), 335 * (0·35), 350 * (0·28)
6-Benzoylphenanthridine [a]	211 (2·80), 250 (3·62), 273 * (1·26), 335 * (0·70), 380 * (0·35)
6-Benzylphenanthridinium chloride	218 (2·71), 252 (3·39), 275 * (1·08), 292 * (0·64), 304 * (0·59), 332 * (0·37), 347 (0·29)
6-Benzyl-5-ethylphenanthridinium iodide	215 (4·04), 254 (4·58), 273 * (1·72), 315 (0·75), 332 * (0·75), 365 * (054)
6-(1-Phenylethyl)phenanthridinium chloride	222 (3·16), 250 (2·80), 280 * (0·56), 293 (0·64), 330 (0·16), 345 (0·16)
6-Benzylphenanthridine 5-oxide	211 (2·79), 231 (2·79), 245 * (2·54), 252 (3·10), 262 * (2·98), 275 * (1·98), 286 * (1·36), 325 (1·18), 365 (0·08)
6-Benzylphenanthridine 5-oxide [a]	211 (2·92), 222 * (2·11), 254 (4·15), 273 * (1·61), 320 (0·93), 375 * (0·37)
6-Benzoylphenanthridine 5-oxide	211 (3·30), 229 (3·16), 237 * (2·86), 250 * (2·65), 287 (1·60), 322 * (1·34), 336 * (1·34), 3·70 * (0·35)
6-Benzoylphenanthridine 5-oxide [a]	209 (2·69), 230 * (3·17), 250 * (2·74), 287 (1·44), 322 * (1·34), 336 * (1·34), 370 * (0·35)
(1)	209 (1·98), 232 (2·51), 242 * (2·28), 252 (2·21), 263 * (1·98), 286 * (1·22), 325 (0·68), 365 (0·06)
(1) [a]	209 (1·91), 243 (2·51), 255 (2·74), 275 * (0·84), 320 (0·61)
(2)	210 (3·06), 230 (3·66), 243 * (3·12), 254 (3·86), 262 (3·66), 273 * (2·45), 286 * (1·40), 323 (1·47), 365 (0·09)
(2) [a]	210 (2·94), 242 * (3·91), 256 (5·38), 272 * (1·83), 320 (1·83), 3·65 (0·18)
(3)	213 (2·40), 222 * (1·88), 253 (4·55), 270 * (2·81), 320 (0·75), 362 (0·55), 378 (0·51), 420 * (0·02)
(3) [a]	213 (2·40), 222 * (1·88), 253 (4·55), 270 * (2·81), 375 (0·71), 390 * (0·70)
(4)	212 (2·72), 221 * (2·21), 254 (5·95), 270 * (3·00), 315 (0·79), 360 * (0·44), 372 * (0·44), 440 * (0·32)
(4) [a]	212 (2·72), 221 * (2·21), 254 (5·95), 270 * (3·00), 360 * (0·64), 370 (0·64), 390 * (0·64)
(5) [b]	205 (2·71), 220 * (2·26), 238 * (3·62), 253 (5·64), 270 * (3·27), 317 (0·88), 363 (0·54), 377 (0·51), 435 (0·06)
(5) [a,b]	205 (2·71), 220 * (2·26), 238 * (3·62), 253 (5·64), 375 (0·54), 390 * (0·45)
(5) [c]	207 (3·88), 220 * (2·75), 238 * (3·81), 254 (5·09), 270 * (3·11), 317 (0·95), 361 (0·56), 380 * (0·53), 430 (0·07)
(5) [d]	206 (3·00), 218 * (2·36), 237 * (3·56), 255 (4·76), 270 * (2·70), 317 (0·73), 361 (0·43), 380 * (0·39), 430 (0·13)
(8)	212 (2·97), 230 * (1·49), 252 * (0·86)
(10)	221 (4·19), 240 * (3·59), 253 * (3·09), 303 (0·83), 330 * (0·48), 350 * (0·56)
(10) [a]	220 (4·19), 253 (2·67), 330 (0·51), 419 (0·77)
(11)	210 (4·21), 250 * (4·89), 264 (5·77), 295 * (2·08), 332 (0·96), 355 * (0·62)
(12)	214 (3·90), 253 (4·98), 265 * (3·57), 277 * (2·87), 290 (2·73), 302 (2·81), 248 (1·47), 365 * (1·30)
(13)	215 (3·31), 240 * (1·22), 265 (6·96), 289 * (2·18), 310 (1·19), 335 * (0·86), 360 * (0·39)
(14)	218 (1·86), 242 * (3·95), 265 (5·79), 289 * (2·64), 310 (0·84), 333 * (0·62), 355 * (0·24)
(15)	215 (3·81), 247 (5·91), 260 * (4·35), 275 (2·72), 290 (2·69), 335 (1·36), 365 (0·47)

* Inflexion.

[a] Spectrum after addition of one drop of 70% perchloric acid. [b] Unresolved mixture. [c] Methanolic solution for isomer with R_F 0·4. [d] Methanolic solution for isomer with R_F 0·25

TABLE 4

Mass spectra [*m/e* values; abundances (%) in parentheses; metastable peaks were observed for transitions shown in square brackets]

(3)	427 (11), 410 (20), 409 (64), 378 (16), 368 (100), 351 (16), 320 (15), 310 (15), 309 (55), 308 (22), 307 (15), 306 (35), 292 (26) 291 (60), 290 (35), 289 (22), 288 (14), 280 (40), 278 (25)
(4)	369 (2), 352 (35), 351 (100), 320 (17), 294 (7), 293 (35), 292 (22), 291 (40), 290 (13), 190 (5), 146 (8) [351 ⟶ 320, 351 ⟶ 293]
(5) [a]	441 (1), 382 (20), 354 (6), 337 (26), 336 (100), 278 (18), 219 (8), 204 (6), 191 (7), 190 (25), 180 (8), 179 (15), 178 (47), 177 (8), 165 (6), 164 (9), 151 (9), 105 (40), 104 (16), 103 (8)
(5) [b]	441 (1), 383 (15), 382 (50), 355 (22), 354 (70) 352 (17), 351 (52), 337 (24), 336 (100), 320 (10), 294 (19), 292 (15), 291 (22), 282 (17), 280 (13), 278 (10), 267 (19), 204 (5), 180 (12), 178 (13), 151 (6) [354 ⟶ 336]
(5) [c]	441 (11), 383 (11), 382 (34), 356 (22), 355 (82), 337 (67), 323 (13), 306 (30), 295 (20), 294 (7), 281 (16), 280 (25), 279 (100), 278 (73), 247 (11), 221 (17), 220 (72), 205 (17), 192 (12), 191 (43), 180 (18), 179 (81), 178 (19), 151 (13), 105 (89)
(10)	506 (50), 505 (100), 504 (50), 475 (8), 427 (13), 414 (28), 413 (50), 411 (10), 398 (7), 397 (18), 383 (9), 247 (8), 246 (11), 218 (5), 208 (13), 204 (5), 189 (6), 180 (4), 166 (20), 152 (10), [506 ⟶ 413, 475 ⟶ 414]
(11)	410 (32), 409 (100), 378 (18), 351 (24), 320 (12), 306 (11), 292 (10), 291 (25), 290 (12), 159 (6), 145 (7) [410 ⟶ 351, 410 ⟶ 320, 320 ⟶ 291]
(12)	352 (30), 351 (100), 320 (15), 294 (8), 293 (40), 292 (31), 291 (51), 290 (19), 289 (10), 190 (6), 146 (6) [351 ⟶ 293, 351 ⟶ 320, 320 ⟶ 292]
(13)	338 (28), 337 (100), 292 (13), 291 (29), 290 (11), 145 (7) [337 ⟶ 292]
(14)	352 (27), 351 (100), 320 (28), 293 (16), 292 (42), 291 (73), 290 (25), 289 (13), 145 (12) [351 ⟶ 292]
(15)	294 (24), 293 (100), 292 (21), 291 (30), 290 (10), 263 (3), 164 (9), 146 (5), 134 (4)

[a] Unresolved mixture. [b] Isomer of R_F 0·4. [c] Isomer of R_F 0·25

TABLE 5

Analytical data

Compound	M.p. (°C) (lit. m.p.)	Yield (%)	λ_{max}/μm (Nujol unless stated)	Found (%) C	H	N	Calc. (%) C	H	N
2-Acetamidobiphenyl	120—122 [a] (119 [b])	78·0							
2-Phenylacetamidobiphenyl	89—91 [c,d] (85—86 [e])	50·0							
2-(2-Phenylpropionamido)-biphenyl	[193—195 at 0·07 mmHg] [f]	90·0	2·96, 3·31w, 3·42w, 5·94s, 6·33, 6·60s, 6·70, 6·93s (film)	83·8	6·5	4·4	83·7	6·4	4·7
2-Diphenylacetamidobiphenyl	152—153 [c,g]	50·0	3·10s, 3·03, 6·07s, 6·25, 6·33w, 6·60s, 6·70s, 6·75	85·7	5·8	4·1	85·9	5·8	3·9
2-Benzylaminobiphenyl	89—90 [h] (89—91 [i])	88·5	2·92, 3·07w, 3·31w, 5·95w, 6·10, 6·30, 6·36s, 6·72s (Kel-F)	88·1	6·5	5·5	88·0	6·6	5·4
6-Benzylphenanthridine	113—113·5 [j,k] (112 [l])	51·0							
6-(1-Phenylethyl)phenanthridine	115—116 [h,j]	67·0	3·38, 3·50w, 6·27, 6·33s, 6·38s, 6·57, 6·73s, 6·85, 6·95s (Kel-F)	89·5	6·3	4·5	89·0	6·1	4·9
6-Diphenylmethylphenanthridine	133—134 [c,g]	54·0		90·2	5·6	4·0	90·4	5·5	4·1
6-Benzoylphenanthridine	151·5—152·5 [m,n] (150—152 [o])	47·0	3·26, 6·00s, 6·21, 6·24, 6·33, 6·72w, 6·83, 6·90s, 6·94s (Kel-F)						
6-Benzylphenanthridinium chloride	232—234 (250—252 [p])	54·0							
6-Benzyl-5-ethylphenanthridinium iodide	179—181	11·0	3·27w, 3·48w, 6·13, 2·21s, 6·30, 6·37, 6·60, 6·70s, 6·89s (Kel-F)	62·5	5·3	3·0	62·1	4·7	3·3
6-(1-Phenylethyl)phenanthridinium chloride	133—135	59·0							
6-Benzylphenanthridine 5-oxide	156—157·5	79·0	3·24w, 3·30w, 6·25, 6·31, 6·37s, 6·57w, 6·70s	84·0	5·5	5·0	84·2	5·3	4·9
6-Benzoylphenanthridine 5-oxide	234—235	65·0	3·24—3·30w, 5·99s, 6·32, 6·61w, 6·72, 6·90s, 6·99 (Kel-F)	80·6	4·2	4·8	80·3	4·4	4·7
(1)	123·5—125 [k,q]	60·0	3·26w, 3·38w, 3·43, 3·56w, 6·11, 6·26, 6·33, 6·42s, 6·73s, 6·90s (Kel-F)	83·3	5·7	4·7	84·3	5·7	4·7
(2)	164—166 [a]	16·5	3·25—3·33w, 6·11w, 6·24, 6·27, 6·41, 6·70s, 6·74s	86·0	5·3	4·0	86·4	5·3	3·9
(3)	191—192 [r]	14·0	3·25w, 3·30w, 3·34, 3·39, 5·77s, 6·00s, 6·20, 6·49s, 6·70, 6·85, 6·94s ($CHCl_3$)	72·9	5·0	3·1	73·1	5·0	3·3
(4)	245—247 [r,s]	14·0	6·03s, 6·20, 6·32s, 6·42s, 6·60w, 6·71, 6·85, 6·96 ($CHCl_3$)	77·3	5·3	3·8	78·0	5·2	3·8
(5) [t]	214—217 [u]	65·0	3·27w, 3·33w, 3·39w, 5·77s, 6·00s, 6·20w, 6·29w, 6·47s, 6·70w, 6·85, 6·94s ($CHCl_3$)	73·5	5·1	3·3	73·5	5·2	3·2
(5) [r]	214—217 [u]		3·27w, 3·34w, 3·39w, 5·77s, 6·00s, 6·21w, 6·29w, 6·37, 6·53s, 6·71w, 6·85, 6·95s ($CHCl_3$)	72·8	5·3	3·4	73·5	5·3	3·2
(8)	139·5—140·5 [k]	70·0	3·27w, 3·37, 3·41, 6·05s, 6·70, 6·78s, 6·90, 6·99 (Kel-F)	82·8	6·4	4·6	83·8	6·7	4·4
(10)	165—166 [w]	10·0	3·27w, 3·37, 3·45—3·55w, 5·35w, 6·30s, 6·70s, 6·77s, 6·90s, 6·97s ($CHCl_3$)	88·0	6·6	5·4	88·1	6·4	5·6
(11)	159—161 [l]	73·0	3·25w, 3·33w, 5·80s, 6·22, 6·45w, 6·61, 6·66, 6·86, 6·93s ($CHCl_3$)	76·3	4·8	3·5	76·3	4·7	3·4
(12)	125—127	15·0	3·24w, 3·33w, 5·87s, 6·23, 6·45w, 6·71, 6·88, 6·75 ($CHCl_3$)	82·5	4·9	4·1	82·0	4·9	4·0
(13)	276—278 [x]	56·0 [y]	3·14—3·62, 5·96s, 6·24, 6·28w, 6·40w, 6·46w, 6·58s, 6·69s	82·2	4·5	4·3	81·9	4·5	4·2
(14)	203·5—204·5 [k,m]	64·0	3·17w, 3·33, 5·85s, 6·23, 6·40, 6·45w, 6·58s, 6·93s, 6·96s ($CHCl_3$)	82·3	5·0	4·2	82·0	4·9	4·0
(15)	95—96	17·0 [z]	3·25w, 3·33, 6·25s, 6·41w, 6·71s, 6·81, 6·91s, ($CHCl_3$)	90·2	4·9	4·8	90·1	5·2	4·8

[a] From ethanol–light petroleum. [b] F. Heusler, *Annalen*, 1890, **260**, 227. [c] Chromatographed prior to recrystallization. [d] From diethyl ether. [e] F. C. Copp and L. P. Walls, *J. Chem. Soc.*, 1960, 312. [f] B.p. [g] From petroleum (b.p. 100—120°). [h] From light petroleum. [i] C. A. Bartram, D. Harrison, and W. F. Short, *J. Chem. Soc.*, 1958, 1158. [j] Purified *via* the hydrochloride which was recrystallised from ethanol. [k] From benzene–light petroleum. [l] C. L. Arcus and M. M. Coombs, *Chem. and Ind.*, 1953, 995. [m] Sublimation. [n] From ethanol. [o] H. Gilman and J. Eisch, *J. Amer. Chem. Soc.*, 1957, **79**, 4423. [p] T. R. Govindachari, B. R. Pai, and V. N. Sundarajan, *J. Chem. Soc.*, 1958, 1715. [q] After drying *in vacuo* at 50°. [r] From chloroform–hexane. [s] After drying *in vacuo* at 105°. [t] Isomer of R_F 0·4. [u] From chloroform–light petroleum. [v] Isomer of R_F 0·25. [w] From benzene–ethanol. [x] From dioxan. [y] By alkaline hydrolysis of (3). [z] By decarboxylation of (21).

200° and 0·05 mmHg for 2 h. The product was collected on a cold finger at −65°; chromatography [elution by diethyl ether–benzene (1 : 4)] gave (3) (14%).

1-*Phenylpyrrolo*[1,2-f]*phenanthridine-2-carboxylic Acid* (13).—(*a*) Compound (3) (3 g) was refluxed with hydrochloric acid (6N; 200 ml) for 7 h. The solid acid (13) was filtered off.

(*b*) Compound (3) (0·5 g) was refluxed with methanol–water (3 : 1; 20 ml) containing sodium hydroxide (4 g) for 15 h. Acidification with hydrochloric acid (4N) precipitated the acid (13).

(*c*) Compound (14) (80 mg) was hydrolysed as described in (*b*).

The samples of (13) obtained by methods (*a*)—(*c*) all had m.p. and mixed m.p. 276—278° (from benzene–ethanol). This acid (13) (360 mg) in tetrahydrofuran (100 ml) at 0° with an excess of ethereal diazomethane gave the ester (14).

Methyl 1-*Phenylpyrrolo*[1,2-f]*phenanthridine-3-carboxylate*

(12).—Compound (4) (1 g) was heated *in vacuo* at 240° and 0·05 mmHg for 1 h. The red product was collected on a cold finger at −65°. Chromatography (elution with light petroleum–benzene) gave the ester (12); further elution with ether–ethanol (4 : 1; 150 ml) gave (4).

1-*Phenylpyrrolo*[1,2-f]*phenanthridine* (15).—(*a*) An intimate mixture of compound (13) (250 mg) with soda-lime (10 g) was heated in a Pyrex tube fitted with an air condenser at 300° for 1·5 h, and then at red heat for 5 min. After cooling, the tube and contents were ground in hot chloroform–methanol (2 : 1; 50 ml) and the solid was filtered off and the soluble material chromatographed. The product (15) was eluted in petroleum.

(*b*) Compound (4) (0·85 g) was refluxed in methanol–water (3 : 1; 40 ml) containing sodium hydroxide (8 g) for 17 h. After acidification (HCl) the solution was extracted with chloroform and the extracts were washed with water and dried. Evaporation gave crude (15), which was chromatographed over silica and eluted with diethyl ether. Samples of (15) obtained by methods (*a*) and (*b*) had m.p. and mixed m.p. 95—96° (from ethanol–light petroleum).

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