729. *Addition Reactions of Heterocyclic Compounds. Part XI.* The Constitution of Some Adducts from Phenanthridine and Dimethyl Acetylenedicarboxylate.*

By R. M. ACHESON and A. O. PLUNKETT.

Phenanthridine and dimethyl acetylenedicarboxylate in benzene gave two 1 : 2 molar adducts and phenanthridine oxalate. The first adduct, tetramethyl 13b*H*-dibenzo[*ac*]quinolizine-1,2,3,4-tetracarboxylate (I), was oxidised to phenanthridone and phenanthridine-6-carboxylic acid, and with hot quinoline gave the corresponding 4*H*-isomer which was converted into methyl 5,6-dihydro-6-oxophenanthridin-5-ylacetate. The oxazine structure (X) of the second adduct was deduced mainly from the spectra of the adduct and its tetrahydro-derivative and is consistent with its reactions. The mode of formation of these adducts and of other products from the acetylenic ester is discussed.

DIMETHYL ACETYLENEDICARBOXYLATE and phenanthridine in methanol give the 1 : 1 : 1 *trans*-adduct (IX) and related compounds are obtained if the solvent contains small

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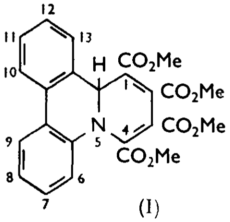
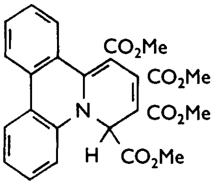
* Part X, *J.*, 1962, 1148.

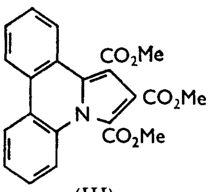
quantities of water.[1] Diels and Thiele,[2] using benzene as solvent, obtained a " labile " yellow 2 : 1 molar adduct of the ester and phenanthridine along with small quantities of a green-yellow isomer, a dibenzoindolizine (III), and an unidentified material of m. p. 150°. Heating the " labile " adduct gave a red " stable " isomer and structures were suggested for these two compounds solely on analogy with those proposed earlier for similar 2 : 1 adducts from the acetylenic ester with pyridine, quinoline, and isoquinoline. The structures of the 2 : 1 adducts of these last three bases having been revised, the products from phenanthridine were re-examined to see if a new structural analogy would hold and in the hope of obtaining information concerning the mechanism of the addition.



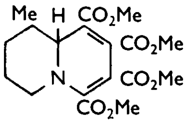
(I)



(II)



(III)



(IV)

The " labile " yellow adduct and the isomeric yellow-green compound, which has been obtained colourless and is henceforth called the white adduct, have been obtained in improved yield from phenanthridine and dimethyl acetylenedicarboxylate in benzene; some phenanthridine oxalate has also been isolated from the residual tar. Boiling the " labile " adduct in quinoline gave the " stable " isomer, as described in outline by Diels and Thiele,[2] but considerable difficulty was experienced in finding satisfactory conditions. Structures for the " labile " and the " stable " phenanthridine adducts corresponding to those currently accepted for similar pyridine,[3] quinoline,[4] and isoquinoline [5] adducts are (I) and (II), respectively, and these are strongly supported by new chemical and physical data.

The " labile " adduct with concentrated hydrochloric acid or ethanolic potassium hydroxide gave some phenanthridine; tetramethyl 9a*H*-quinolizine-1,2,3,4-tetracarboxylate and concentrated hydrobromic acid, or alkali, similarly gives pyridine.[6] Oxidation of the " labile " adduct with potassium permanganate in acetone, under conditions which were separately shown not to affect phenanthridine, gave phenanthridone and a smaller proportion of a complex mixture of acids. The acid-insoluble but sodium hydroxide-soluble fraction of this mixture, which could not be resolved further, had the ultraviolet and infrared absorption spectrum characteristics expected of an *N*-substituted 5,6-dihydro-6-oxophenanthridinecarboxylic acid. This mixture was also shown to contain phenanthridine-6-carboxylic acid by paper chromatographic and electrophoretic comparison with a pure sample obtained by oxidation of 6-styrylphenanthridine. Attempts to obtain an analytically pure sample of this acid from the described[7] chromic acid oxidation of 6-(1,3-dihydroxy-2-propyl)phenanthridine were unsuccessful although paper chromatography showed that the product contained much of the desired material. These results strongly suggest that the " labile " adduct contains the intact phenanthridine skeleton with an additional ring spanning the 5,6-positions.*

The infrared absorption spectrum of the " labile " adduct (I) has the maxima in the 5—7 μ region characteristic of the " labile " adducts derived from other pyridines.[5] The

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* I.U.P.A.C. (Ring Index) numbering: N = 5.

[1] Acheson and Bond, *J.*, 1956, 246.

[2] Diels and Thiele, *J. prakt. Chem.*, 1940, **156**, 195.

[3] Acheson and Taylor, *Proc. Chem. Soc.*, 1959, 186; *J.*, 1960, 1691.

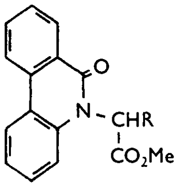
[4] Acheson, Earl, Higham, Richards, Taylor, and Vernon, *Proc. Chem. Soc.*, 1960, 281.

[5] Acheson and Hole, *J.*, 1962, 748.

[6] Diels, Alder, Friedrichsen, Petersen, Brodersen, and Keck, *Annalen*, 1934, **510**, 87.

[7] Walls, *J.*, 1934, 104; Ritchie, *Proc. Roy. Soc. N.S.W.*, 1944, **78**, 164.

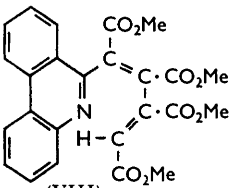
long-wavelength absorption maximum (410 mμ) of the " labile " adduct is at shorter wavelengths than those of the " labile " adducts from 3-methylisoquinoline (420 mμ) and isoquinoline (438 mμ), this series reflecting decreasing steric hindrance in the adducts. The ultraviolet and visible absorption spectrum of the " labile " adduct is remarkably similar to that of the tetrahydro-9a*H*-9-methylquinolizine [3] (IV) but has an additional maximum at 258 mμ. If the 258 mμ maximum is due to the carbocyclic rings it appears that the spectrum of the " labile " adduct (I) is built up of two separate chromophores and is consistent with the presence of a hydrogen atom at position 13b. A Dreiding model of the adduct showed that the carbocyclic rings subtend very substantial angles to the nitrogen–ester system and small angles to each other; the long-wavelength maxima of 3,3′- and 4,4′-dimethylbiphenyl are at *ca.* 255 mμ (ε *ca.* 10^4).[8] Although the " labile " adduct, like all other " labile " adducts previously examined, did not react with perchloric acid in acetic acid, reversible salt formation in concentrated sulphuric or perchloric acid was demonstrated as the new absorption spectrum obtained in these solvents reverted to that of the adduct itself on dilution with methanol.



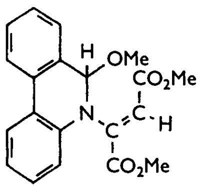
(V; R = H)

(VI; R = $CO{\cdot}CO_2H$)

(VII; R = $CO{\cdot}CO_2Me$)



(VIII)



(IX)

Oxidation of the " stable " adduct with potassium permanganate in acetone gave phenanthridone and small quantities of the keto-acid (VI), a compound presumed to be the dimethyl ester (VII), and an unidentified substance. These compounds had typical phenanthridone-type ultraviolet absorption spectra and an absorption maximum at *ca.* 6·03 μ which is possessed by phenanthridones and can be attributed to the carbonyl group. The dimethyl ester (VII) decomposed on attempted purification, but was also obtained from the keto-acid (VI) with diazomethane. The keto-acid (VI), when heated alone or, better, with acetic anhydride, gave methyl 5,6-dihydro-6-oxophenanthridin-5-ylacetate (V) which was identical with a specimen synthesised from phenanthridone and methyl bromoacetate. Attempted decarboxylation of the unidentified substance gave a complex mixture containing the acetate (V), detected chromatographically. The identified phenanthridones can be accounted for readily on the proposed formulation (II) for the " stable " adduct. All the oxidation fractions were examined chromatographically for phenanthridine-6-carboxylic acid which would be expected as an oxidation product of the open-chain structure (VIII) but no trace of it was detected.

The long-wavelength absorption maxima of the "stable" adducts (4*H*-quinolizines) obtained from several pyridines are at 439—445 mμ (ε 9700—12,900),[3] from quinoline at 459 (ε 13,900)[4] from isoquinolines at 464—469 (14,000—16,600),[5] and from phenanthridine at 466 mμ (ε 13,600). This series shows that adding the first, but not a subsequent, benzene ring to the " stable " pyridine adduct structure causes a small increase in conjugation, and also suggests that the major visible chromophore is closely connected with a common structural characteristic of the adducts and not with the original heterocyclic base which combined with the dimethyl acetylenedicarboxylate. The last conclusion is supported by the marked similarities in the infrared absorption spectra of the adducts. Elvidge and Jackman,[9] on the basis of some nuclear magnetic resonance spectrum measurements, have suggested that the " stable " pyridine adducts may be mixtures of ring–chain tautomers

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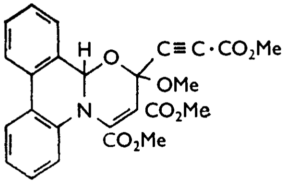
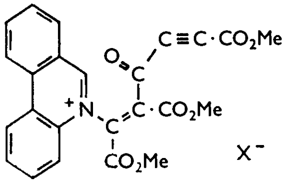
[8] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," Wiley and Sons, New York, 1951.

[9] Elvidge and Jackman, *J.*, 1961, 859.

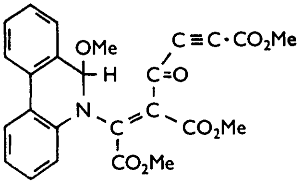
(*e.g.*, II and VIII) between which equilibrium is very rapidly established and is well towards the open-chain form. This interpretation is not in agreement with the ultraviolet results as it could hardly be expected that pyridines, quinoline, isoquinolines, and phenanthridines with the same auxochromic substitutent replacing a hydrogen atom *ortho* to the hetero-atom would have such similar ultraviolet and visible absorption spectra.



(X)



(XI)



(XII)

The possibility that a change in constitution of the " stable " adducts occurs in the comparatively concentrated solutions used for the nuclear magnetic resonance studies is unlikely as, in chloroform, tetramethyl 7,9-dimethyl-4*H*-quinolizine-1,2,3,4-tetracarboxylate possesses an absorption spectrum very similar to that[3] for methanol and obeys Beer's Law over the whole spectrum within the limitations of our Cary recording spectrophotometer (10^{-3} to 2×10^{-5}M-solutions).

It has been established, by nuclear magnetic resonance spectroscopy, that the " stable " pyridine adducts have substantial ring currents,[3,9] and, as diethyl 1,2-dihydro-1,4,6-trimethyl-2-methylenepyridine-3,5-dicarboxylate does not, Elvidge and Jackman concluded that the " stable " adducts cannot have an apparently structurally analogous bicyclic structure (*e.g.*, II). However, this does not necessarily follow[10] for the " stable " adducts are vinylogous pyridones in two senses and pyridones also possess ring currents.[9]

The " stable " phenanthridine adduct is a weaker base than corresponding quinoline and isoquinoline adducts, but it formed a crystalline perchlorate and was converted reversibly into the cation by concentrated sulphuric acid. As in the isoquinoline series, the ultraviolet data suggest that the proton adds to a substantial extent at position 1, although appreciable addition at position 3 is not excluded.

The ultraviolet absorption spectra of the white adduct (X) and its tetrahydro-derivative (XIII) showed the presence of a very different type of chromophore from those in the " labile " (I) and the " stable " (II) adduct. They closely resembled that of the dihydrophenanthridine (IX) which is in equilibrium with the conjugate phenanthridinium methoxide.[1] In methanol the equilibrium greatly favours form (IX), as sodium methoxide causes no change in absorption spectrum but acidification causes a large reversible change to a phenanthridinium type; the white adduct (X) is exactly analogous but the corresponding cation (XI) rapidly decomposes.

Oxidation of the white adduct with potassium permanganate gave mainly phenanthridone along with traces of the phenanthridone-carboxylic acid (VI) obtained earlier on oxidation of the " stable " adduct (II). When alkaline potassium ferricyanide was the oxidant the only product identified was phenanthridine. No phenanthridine-6-carboxylic acid could be detected chromatographically in the products of these oxidations. Hydrogenation of the white adduct gave a tetrahydro-derivative (XIII) and 5,6-dihydrophenanthridine, which was characterised as phenanthridine picrate. The white adduct must therefore possess a phenanthridine ring linked directly to carbon atoms only through position 5; hydrogenation of the betaine derived from (IX) gives 5,6-dihydrophenanthridine.[1]

The white adduct has infrared maxima corresponding to the presence of a disubstituted acetylene (4·46 μ) and carbonyl groups (5·77 and 5·81 μ) similar to those of both dimethyl

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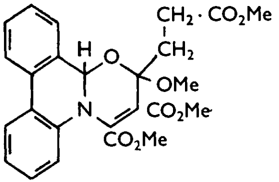
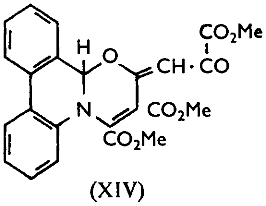
[10] Acheson, " Advances in Heterocyclic Chemistry," Vol. I, ed. Katritzky, Academic Press, in the press.

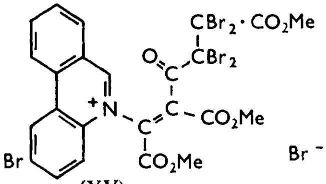
acetylenedicarboxylate (5·79 μ) and the dihydrophenanthridine ester (IX) (5·77 and 5·81 μ). There is also a maximum at 13·34 μ which is in the region where a considerable number of 2-alkynecarboxylic esters also possess maxima.[11] The infrared absorption spectrum of the tetrahydro-derivative (XIII) was very similar except that the maxima at 4·46 and 13·34 μ were absent. An alternative formulation (XII) for the white adduct is excluded as neither it nor its tetrahydro-derivative possesses an absorption maxima at *ca.* 6 μ which would be expected of the conjugated ketonic group on analogy with other ethylenic and acetylenic ketones.[12] The white adduct also did not react with 2,4-dinitrophenylhydrazine in cold methanolic sulphuric acid, but, when heated, gave a deep red product which resisted attempts at purification.



(XIII)



(XIV)



(XV)

The white adduct was too sparingly soluble for its nuclear magnetic resonance to be measured in the usual solvents, but that of the tetrahydro-derivative (XIII) in carbon tetrachloride was obtained by using a high-resolution spectrometer [13] at 30 Mc./sec. and interpreted for us by Dr. P. Higham. Resonance occurred at 7·0—7·3 p.p.m. (τ scale) in the region of CH_2 bonded to carbon. The intensity suggested one CH_2 only and the unsymmetrical shape indicated that it was half of an A_2B_2 type of spectrum. The other part was mostly beneath the methyl resonance at 5·7 and 6·05—6·10 p.p.m., and its shift to low field would be caused by the adjacent ester group. A single line at 3·8 p.p.m. is from the single proton which has no neighbouring CH groups to split the resonance. From work on pyridine [3] and quinoline [4] adducts the line position indicated that this proton is close to a nitrogen atom and/or a benzenoid ring. The single proton in structure (XIII) fulfils these requirements. It is known [3] that the methyl resonances of ester-methyl groups on carbon β to nitrogen atoms in conjugated systems occur at higher fields than those of corresponding α-ester methyl groups and also that esters on saturated carbon atoms occur at the same higher field; the methyl resonance for the compound (XIII) fall into two groups: the peaks at the higher fields (6·05 and 6·10 p.p.m.) are due to the terminal ester and the ester group β to the nitrogen, while that at 5·7 p.p.m. is due to superposition of the CH_3 groups of the α-ester and the methoxyl groups. A series of lines between 1·3 and 3 p.p.m. is due to aromatic protons.

Refluxing the white adduct (X) with ethanol, in an attempt to replace the angular methoxyl by an ethoxyl group, gave a glass which possessed no acetylenic infrared absorption. Treating the adduct (X) with methanolic perchloric acid, in the hope of obtaining the perchlorate (XI; $X = ClO_4^-$), gave a pale yellow compound $C_{21}H_{10}NO_5(OMe)_3$. Structure (XIV), which could be formed from the white adduct by hydration of the triple bond followed by loss of the angular methoxyl group which is β to the newly formed carbonyl group, is in agreement with the analytical data, the ultraviolet absorption spectrum which shows more conjugation than that present in the white adduct (X), and the infrared absorption spectrum which shows no absorption in the triple-bond region, and the appearance of a highly conjugated carbonyl group ($\nu_{max.}$ 6·0 μ). This new carbonyl group is a part of a vinylogous ester system and its failure to react with 2,4-dinitrophenylhydrazine is therefore understandable.

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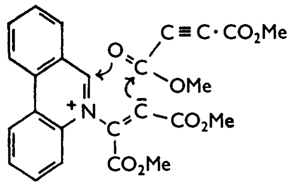
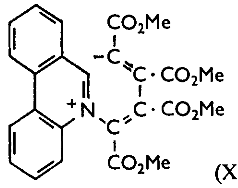
[11] Allan, Meakins, and Whiting, *J.*, 1955, 1878.
[12] Jones, Humphries, and Dobriner, *J. Amer. Chem. Soc.*, 1950, **72**, 956.
[13] Leane, Richards, and Schaefer, *J. Sci. Instr.*, 1959, **36**, 230.

The white adduct (X) with bromine gave an unstable product possessing an ultraviolet absorption spectrum of phenanthridinium type and in the infrared region no acetylenic absorption but a new maximum at 5·90 μ consistent with the presence of an ethylenic ketone grouping.[14] As attempted crystallisation from dioxan caused decomposition and subsequent basification gave the known 2-bromophenanthridine[15] the unstable product is formulated as (XV).

The formation of all the recognised types of adduct from phenanthridine and dimethyl acetylenedicarboxylate can be accounted for on the assumption that an initial Michael-type reaction leads to the zwitterion (XVI). This by successively adding a proton and a methoxide ion as indicated earlier[1] can give the 1 : 1 : 1 molar adduct (IX). Reaction of the negatively charged carbon atom of (XVI) with the carbonyl group of another molecule of the acetylenic ester and cyclisation as shown leads to the white adduct (X), while reaction at the triple bond will give the zwitterion (XVII) which can cyclise to the " labile " adduct (I).

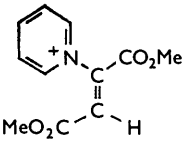


(XVI)

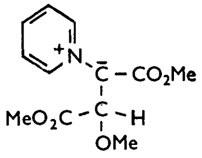


(XVII)

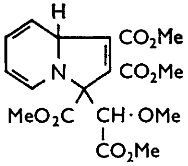
Pyridine and dimethyl acetylenedicarboxylate in methanol give trimethyl indolizine-1,2,3-tricarboxylate[16] and the methoxymethylindolizine (XXI)[17] but no mechanism has been suggested. The formation of both compounds in the same reaction can be accounted for if the pyridine combines successively with the ester and a proton, giving an ion (XVIII) which then adds a methoxide ion forming (XIX); addition of methoxide to the ring would not be expected as equilibria between *N*-substituted pyridinium hydroxides and corresponding 1,2-dihydropyridines usually favour the ionic form.[18] Further addition of dimethyl acetylenedicarboxylate and cyclisation leads to (XX) which can aromatise either to trimethyl indolizine-1,2,3-tricarboxylate or to (XXI); the dibenzoindolizine (III) could be formed by such a sequence. The general scheme is supported by the observation[19] that pyridine and dimethyl acetylenedicarboxylate in ether gave trimethyl indolizine-1,2,3-tricarboxylate only when the ether contained traces of ethanol.



(XVIII)



(XIX)



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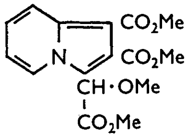

(XXI)

EXPERIMENTAL

Infrared absorption spectra were measured in paraffin paste (P) or in chloroform (C) and are usually only given for the 4—7 μ region. Ultraviolet absorption spectra are recorded in

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[14] Theus, Surber, Colombi, and Schinz, *Helv. Chim. Acta*, 1955, **38**, 239.

[15] Gilman and Eish, *J. Amer. Chem. Soc.*, 1955, **77**, 6379.

[16] Diels and Meyer, *Annalen*, 1934, **513**, 129.

[17] Crabtree, Johnson, and Tebby, *J.*, 1961, 3497.

[18] Acheson, " Introduction to the Chemistry of Hetercyclic Compounds," p. 165, Interscience, Publ., Inc., New York, 1960.

[19] Wiley and Knabeschuh, *J. Org. Chem.*, 1953, **18**, 836.

the Table and below; they were measured for methanol solutions unless specified and recorded in mμ (ε × 10^{-4} being given in parentheses). Inflexions are marked with an asterisk. Whatman No. 1 paper was used for chromatography, carried out by the ascending technique, and for electrophoreses. Solvent A was propan-2-ol–ammonia (*d* 0·88)–water (8 : 1 : 1 v/v), and solvent B was butan-1-ol–acetic acid–water (4 : 1 : 1). The papers were examined under a Hanovia lamp emitting 90% of its radiation at 2537 Å, and were sprayed with 1% aqueous ferric chloride.

6-*Styrylphenanthridine*.—6-Methylphenanthridine[20] (5·0 g.), benzaldehyde (2·7 g.), and anhydrous zinc chloride (0·82 g.) were heated at 195° for 3 hr. After cooling, water (30 ml.) was added and the solid product (7·83 g.) collected. Crystallisation from ethanol (110 ml.; charcoal) gave 6-styrylphenanthridine (4·0 g.) as colourless prisms, m. p. 133° (Found: C, 89·5; H, 5·4; N, 4·7. Calc. for $C_{21}H_{15}N$: C, 89·7; H, 5·3; N, 5·0%). Ritchie[21] cyclised 2-cinnamamidobiphenyl and gave m. p. 133°. Concentration of the mother-liquid gave a second solid, which after extraction with boiling nitromethane gave a few mg. of a compound which was probably 1,3-di(phenanthridin-6-yl)-2-phenylpropane, $(NC_{13}H_8{\cdot}CH_2)_2CHPh$, colourless crystals (from dioxan), m. p. 211—212° (Found: C, 87·6; H, 5·6%; *M*, 485). $C_{35}H_{26}N_2$ requires C, 88·6; H, 5·5%; *M*, 474).

Absorption spectra.

Phenanthridine derivatives	Solvent†	Absorption maxima (mμ) (10^{-4} ε in parentheses)							
The 13b*H*-dibenzo[*ac*]-quinolizine (I)	M	410	(0·78)	293 *	(1·27)	258	(3·42)	229	(1·69)
	S or P[1]	416	(0·52)	369 *	(0·41)	318	(1·63)	274	(2·49)
The 9a*H*-quinolizine (IV)	M	411	(0·58)	286	(1·48)	231	(1·20)		
The 4*H*-dibenzo[*ac*]-quinolizine (II)	M	466	(1·36)	330 *	(0·97)	303	(1·17)	260	(4·05)
	S[1] or P	396	(0·51)	350	(0·69)	290 *	(0·75)	260 *	(3·14)
		251	(5·32)						
The white adduct (X)	D	328	(1·16)	275	(1·67)				
	M[2]	345 *	(1·08)	330	(1·15)	276	(1·64)	268 *	(1·57)
		232	(2·27)						
	MA[3]	364	(0·63)	296 *	(0·87)	263	(1·57)		
	S[4]	333	(1·37)	253	(6·96)				
The tetrahydro-white adduct (XIII)	M[2]	323	(1·07)	270	(1·70)	264 *	(1·56)	234 *	(2·13)
	MA[4]	375 *	(0·47)	331	(0·90)	249	(4·37)		
	MB[5]	458	(0·53)	335	(0·67)	274	(1·30)	269	(1·26)
		267	(1·21)	240	(2·06)				
	MB[6]	329	(0·85)	267	(3·06)	260	(3·12)	250 *	(3·47)
		246	(3·53)	240 *	(3·47)				
The triester (XIV)	M	393	(0·64)	280	(2·79)	252	(1·93)		
	MA	409	(0·70)	293 *	(1·86)	267	(3·27)		
	MB	386	(0·58)	310 *	(1·49)	277	(3·07)	250	(2·12)
Hexabromo-derivative (XV)	M	379	(0·95)	347	(0·71)	310	(0·60)	293 *	(0·74)
		247	(2·87)						
	MA[4]	360 *	(0·54)	321	(0·84)	249	(4·11)		
	MB[4]	380—360 *	(0·54)	347	(0·71)	331	(0·73)	293	(0·98)
		248	(4·10)						
The indolizine (III)	M	323 *	(0·97)	265	(5·00)	250 *	(3·81)		
6-Styrylphenanthridine	M	330	(1·58)	249	(3·83)				
	MA	392	(1·65)	332 *	(1·38)	250	(3·9)		
6-Methylphenanthridine	M	347	(0·33)	332	(0·33)	297 *	(0·78)	273 *	(1·35)
		250	(5·5)						
	MA	364	(0·66)	352	(0·66)	315	(1·03)	279	(1·03)*
		251	(5·8)						
2-Bromophenanthridine	M	347	(0·33)	331	(0·30)	316 *	(0·24)	303 *	(0·72)
		293	(0·84)	274 *	(0·97)	249	(5·11)		
	MA	364	(0·58)	348	(0·60)	322	(0·78)	284	(0·45)
		256 *	(3·4)	249	(4·22)				
The dihydrophenanthridine (IX)[7]	M	330	(0·80)	274 *	(1·27)	267	(1·43)	232	(2·90)
	MA	368	(0·56)	329	(0·85)	250	(5·01)		
1,3-di(phenanthridin-6-yl)-2-phenylpropane	M	346	(0·31)	331	(0·33)	290 *	(0·94)	272 *	(1·72)
		246	(6·65)						
	MA	372	(0·67)	321	(0·88)	249	(6·12)		
Phenanthridine-6-carboxylic acid	M	345	(0·25)	329	(0·29)	249	(4·95)		
	MA	325—338 *	(0·55)	307	(0·56)	251	(4·54)	209	(1·99)

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[20] Morgan and Walls, *J.*, 1931, 2447.

[21] Ritchie, *Proc. Roy. Soc. N.S.W.*, 1944, **78**, 147.

Phenanthridine derivatives	Solvent†	Absorption maxima (mμ) (10^{-4} ε in parentheses)							
Phenanthridones									
Unsubstituted	M	335	(0·74)	321	(0·85)	308	(0·60)	300 *	(0·55)
		257	(1·91)	249	(1·63)				
5-Methyl	M	337	(0·72)	322	(0·84)	310 *	(0·57)	300	(0·47)
		258	(1·90)	249	(1·65)				
-5-maleic acid [7]	MA	337	(0·65)	322	(0·79)	310 *	(0·59)	302 *	(0·54)
		260	(1·80)	250 *	(1·83)				
	MB	339	(0·75)	324	(0·89)	313 *	(0·65)	302 *	(0·61)
		260	(2·10)	250 *	(2·10)				
-5-fumaric acid [7]	MA	334	(0·48)	321	(0·62)	310 *	(0·50)	300	(0·48)
		270 *	(1·00)	258	(1·60)	237	(4·26)	230	(4·35)
	MB	339	(0·50)	324	(0·60)	313 *	(0·46)	301 *	(0·42)
		269 *	(0·87)	259	(1·59)	250 *	(1·54)	236 *	(3·98)
		232	(4·10)						
The ester (V)	M	337	(0·68)	322	(0·78)	310 *	(0·54)	300 *	(0·48)
		270 *	(1·80)	260	(1·67)	250	(1·44)	238	(4·36)
		231	(4·50)						
The keto-acid (VI)	M	339	(0·71)	324	(0·92)	290	(1·53)	270 *	(2·12)
		261	(2·66)	251	(2·12)	239	(4·80)	232	(4·93)
	MA	335	(0·68)	321	(0·82)	310 *	(0·63)	300 *	(0·64)
		268 *	(1·69)	259	(2·56)	250	(2·49)	237	(5·56)
		231	(5·65)						
	MB	340	(0·80)	325 *	(1·08)	299	(1·72)	269 *	(1·95)
		261	(2·49)	252	(2·04)	238	(4·80)	232	(4·90)

Unless stated, changes effected by acid or alkali are reversible.

* Inflexion. † A = Acidified with sulphuric acid. B = basified with sodium methoxide. D = dimethylformamide. M = methanol. P = 72% perchloric acid. S = concentrated sulphuric acid.

[1] On immediate dilution with methanol, the spectrum reverts to that obtained in methanol. [2] No change on basification. [3] Reversible on immediate basification. [4] Not reversible. [5] After previous acidification. [6] As (5), 18 hr. later. [7] Prepared as described in ref. 1.

Phenanthridine-6-*carboxylic Acid*.—6-Styrylphenanthridine (1·72 g.) was added to potassium permanganate (2·65 g.) in refluxing acetone (100 ml.). After 2 hr. the colour had disappeared and a further 0·2 g. of oxidant in acetone (100 ml.) was added and refluxing continued for 30 min. The acetone was removed *in vacuo*, water added, and sulphur dioxide passed in to dissolve the manganese dioxide. After cooling, the yellow precipitate [1·05 g., m. p. 162° (decomp.)] was collected and extracted with hot concentrated hydrochloric acid (15 ml.). The residue was boiled with water, collected [0·27 g., m. p. 167° (decomp.)], and crystallised from glacial acetic acid, yielding phenanthridine-6-carboxylic acid as yellow rhombs which on storage over sodium hydroxide *in vacuo* became colourless; they had m. p. 167° (decomp.) (Found: C, 75·5; H, 4·2; N, 6·2. Calc. for $C_{14}H_9NO_2$: C, 75·4; H, 4·0; N, 6·3%) [lit.,[7] m. p. 155° (decomp.)]. A few mg. were heated to 170°; then vigorous effervescence took place for about a minute. The product, after crystallisation from ethanol, had m. p. 108° alone or mixed with phenanthridine.

6-Methylphenanthridine was not oxidised by potassium permanganate in boiling acetone and, although some oxidation occurred in 2N-sulphuric acid,[22] only starting material could be recovered. Phenanthridone (20%) and phenanthridine-6-carboxylic acid (5%) were obtained by using sodium dichromate in 2N-sulphuric acid at 100°.

Reaction of Phenanthridine and Dimethyl Acetylenedicarboxylate.—The ester (26·8 ml.) was added to phenanthridine (20 g.) in benzene (40 ml.) at *ca.* 5°; a dark yellow colour appeared, much heat was evolved, and a precipitate was formed. After initial cooling in ice–water and subsequent storage at room temperature for 90 min. the mixture was refluxed for 80 min., then cooled at 0°, and the yellow precipitate was collected, washed with benzene, and dried. It was then refluxed for 1 hr. with two portions of acetonitrile (120 + 60 ml.); the insoluble material was almost pure *tetramethyl* 13*b*H-*dibenzo*[ac]*quinolizine*-1,2,3,4-*tetracarboxylate*, the "labile" yellow adduct (I). It separated from glacial acetic acid in yellow needles, m. p. 284° (decomp.) (Found: C, 64·5; H, 4·7; N, 3·0; OMe, 26·8. $C_{25}H_{21}NO_8$ requires C, 64·8; H, 4·5; N, 3·0;

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[22] Cf. Singer and McElvain, in *Org. Synth.*, Coll. Vol. III, p. 740.

4OMe, 26·8%) [lit.,[2] for the same product given a different structure, m. p. 280° (decomp.)], $\nu_{max.}$ (P) 5·76, 5·83, 5·89, 6·21, 6·62, 6·85, and 6·96 μ. It dissolved in cold concentrated sulphuric acid and after 10 min. was precipitated unchanged in 98% yield on dilution with ice–water. It was unaffected by methyl sulphate in refluxing nitromethane, but in refluxing nitrobenzene charring occurred.

Concentration of the combined acetonitrile extracts gave *dimethyl 2-methoxy-2-methoxycarbonylethynyl-*2,13*b*H-[1,3]-*oxazino*[2,3-f]*phenanthridine-*3,4-*dicarboxylate*, the white adduct (X) (2·47 g., 5%), which separated from acetonitrile in hexagons, m. p. 193—194° (Found: C, 64·4; H, 4·7; N, 3·4; OMe, 26·0. $C_{25}H_{21}NO_8$ requires C, 64·8; H, 4·5; N, 3·0; 4OMe, 26·8%) [lit.,[2] for the same product, given a different structure, m. p. 196° (decomp.)], $\nu_{max.}$ (C) 4·46, 5·77*, 5·81, 6·24, 6·40, 6·70, 6·89, and 6·99 μ. No further white adduct was extracted from the almost pure " labile " adduct by more acetonitrile. Dimethyl *trans*-5,6-dihydro-6-methoxyphenanthridin-5-ylfumarate (IX) showed $\nu_{max.}$ (C) 5·80, 6·10*, 6·22, 6·40, 6·68, 6·71, and 6·99 μ.

Evaporation of the benzene filtrate from the original reaction mixture left a dark brown tar which failed to crystallise, but after 3 years was treated with chloroform, giving a residual solid. Crystallisation from aqueous methanol (1 : 1) gave *phenanthridine oxalate monohydrate* (Found: C, 63·1; H, 4·8; N, 5·0. $C_{15}H_{11}NO_4,H_2O$ requires C, 62·8; H, 4·5; N, 4·9%) as colourless needles, m. p. 166° alone and mixed with a sample prepared from phenanthridine and oxalic acid. The infrared absorption spectra (P) of the two samples were identical.

Degradations of Tetramethyl 13*b*H-*Dibenzo*[ac]*quinolizine*-1,2,3,4-*tetracarboxylate* (I).—(i) *Oxidation*. The " labile " adduct (I) (15 g.), potassium permanganate (60 g.), and acetone (2 l.) were refluxed for 1 hr. and the acetone was removed *in vacuo*. A control experiment showed that phenanthridine was unaffected under these conditions. Water was added and the distillation continued for a short time to ensure removal of all acetone. A small quantity of phenanthridine, m. p. and mixed m. p. 105—106°, separated from the distillate. Sulphur dioxide was then passed into the involatile mixture until all the manganese dioxide had dissolved. The residual yellow solid (7·8 g.) was collected and extracted with cold 2·5N-aqueous sodium hydroxide (2 × 25 ml.), and the residue (5·57 g.) was washed with water. This residue was then extracted with aqueous hydrochloric acid (30 ml. of *d* 1·16; with 70 ml. of water). The insoluble material [4·53 g.; m. p. *ca.* 224° (decomp.)], after two crystallisations from ethanol, had m. p. 284° (decomp.) (1·0 g.) alone or mixed with authentic phenanthridone; the infrared absorption spectra of the materials were identical. The sodium hydroxide extract was treated with concentrated hydrochloric acid until precipitation of a yellow-brown tarry solid [1·0 g.; m. p. 85—110° (decomp.)] was maximal. This was collected, washed with water, and then treated with concentrated hydrochloric acid (25 ml.). A sticky insoluble material was centrifuged off and the supernatant liquid diluted with an equal volume of water and cooled, a dark yellow-brown solid being precipitated. From the mother-liquor a further brown solid [A; m. p. 165—178° (decomp.)] was slowly precipitated, and chloroform extraction of the filtrate gave a brown solid (B; m. p. 100—105°).

Authentic phenanthridine-6-carboxylic acid appeared yellow on chromatograph paper when examined under ultraviolet light, and spraying with aqueous ferrous ammonium sulphate gave a purple-red colour (changing to yellow) in daylight. The R_F's in (*a*) the organic phase of butan-1-ol–acetic acid–water (4 : 1 : 5 v/v), (*b*) solvent A, (*c*) solvent A but with an 8 : 2 : 1 ratio, (*d*) as (*c*) 8 : 0·1 : 1·9 ratio, and (*e*) the organic phase of benzene–propionic acid–water (2 : 2 : 1) were 0·66, 0·52, 0·80, 0·37, 0·85.

Both solids A and B were chromatographed alongside the authentic acid in these five solvents and both showed the presence of a compound at the same position and with the same characteristics as those of the authentic acid. In addition, both solids A and B clearly contained at least six further compounds, some of which gave colours with ferrous ammonium sulphate.

(ii) *Decomposition with concentrated hydrochloric acid*. The " labile " adduct (0·65 g.) and concentrated hydrochloric acid (4·5 ml.) were heated in a sealed tube to 200° for 4·5 hr. The charred product was washed out with water (20 ml.), the washings were filtered, and treated with charcoal, and the resulting bright yellow solution was basified. Extraction of the brown precipitate (180 mg.) with ether gave phenanthridine (55 mg.), m. p. and mixed m. p. 108°. Another portion (0·65 g.) of the same sample of " labile " adduct was exhaustively extracted with refluxing methyl cyanide, and the soluble material successively transferred to chloroform and to 2N-hydrochloric acid. Examination of the extinction at 315 mμ showed that the original sample of labile adduct must have contained less than 1·1 mg. of phenanthridine.

(iii) *Hydrolysis with potassium hydroxide.* The " labile " adduct was recovered (88%) after 8 hr. in refluxing 20% aqueous potassium hydroxide. Refluxing the adduct (1 g.) in methanol (16 ml.), water (4 ml.), and potassium hydroxide (4 g.) for 8 hr. and cooling gave a deep red precipitate. This dissolved on addition of water (50 ml.). The methanol was evaporated, and the aqueous solution was extracted with ether. Evaporation of the dried extract gave phenanthridine (50 mg.), m. p. and mixed m. p. 106—108°.

Trimethyl Dibenzo[e,g]*indolizine*-1,2,3-*tricarboxylate* (III).—The " labile " adduct (I) (1·07 g.) in acetic acid (50 ml.) was heated on a steam-bath for 3·5 hr. with an excess of manganese dioxide, freshly prepared from potassium permanganate and manganese sulphate. After filtration and concentration water was added and the precipitate (0·43 g.) collected. Crystallisation from methyl cyanide to constant m. p. gave the indolizine as colourless rods, m. p. 218° (Found: N, 3·5; OMe, 23·7. Calc. for $C_{22}H_{17}NO_6$: N, 3·6; 3OMe, 23·8%). Diels *et al.*[2] give m. p. 224° for a sample prepared from the " stable " adduct (II) with chromic acid in acetic acid; these conditions did not affect the " labile " adduct.

Tetramethyl 4H-*Dibenzo*[ac]*quinolizine*-1,2,3,4-*tetracarboxylate* (II).—(i) The " labile " adduct (I) (20 g.) and redistilled quinoline (50 ml.) were heated at 140° for 1 hr.; a deep red-brown colour formed after a few minutes. After cooling, the product was poured into water (200 ml.) containing concentrated hydrochloric acid (50 ml.) with stirring. The deep red precipitate (17·1 g.; m. p. 210—220°) was collected, washed with water, dried, and extracted with refluxing methanol (60 ml.). The insoluble material (11·1 g.; m. p. 237—238°) was refluxed with methyl cyanide (400 ml.): both the undissolved material (4·5 g.) and the material which separated on cooling (4·12 g.) were the almost pure 4H-*dibenzoquinolizine*, the " stable " adduct (II), and a further quantity was obtained on concentration of the filtrate. It separated from methyl cyanide in red polyhedra, m. p. 245° (decomp.) (Found: C, 64·6; H, 4·7; N, 3·5; OMe, 26·0. $C_{25}H_{11}NO_8$ requires C, 64·8; H, 4·5; N, 3·0; 4OMe, 26·8%) [lit.,[2] for same product given a different structure, m. p. 245° (decomp.)], $\nu_{max.}$ (P) 5·75, 5·89, 5·97, 6·25, 6·41, 6·70, 6·86, and 7·01 μ, $\nu_{max.}$ (C) 5·76, 5·97, 6·22, 6·30, 6·41, 6·70, 6·86, and 7·00 μ. Many other reaction times and temperatures were tried with less satisfactory results. In one experiment with refluxing pyridine a 59% yield of the crude product was obtained, but it proved much more difficult to purify than the product of the quinoline reaction. It is particularly noteworthy that the decomposition point of the stable adduct is not depressed by admixture with even considerable quantities of the labile adduct (I), but the infrared absorption spectra of these isomers in paraffin paste differ considerably and this criterion was always used in assessing purity.

The 4*H*-dibenzoquinolizine (II) (50 mg.) dissolved in concentrated sulphuric acid (2·5 ml.) and after 10 min. dilution with ice–water (20 ml.) precipitated the original compound almost quantitatively.

The 4*H*-dibenzoquinolizine (II) (52 mg.) in glacial acetic acid (1 ml.) with 60% perchloric acid (0·2 ml.) gave the *perchlorate* (39 mg.), as yellow needles, m. p. 187° (decomp.) (Found: C, 53·2; H, 4·0; Cl, 6·8. $C_{25}H_{22}ClNO_{12}$ requires C, 53·3; H, 3·9; Cl, 6·3%), that was hydrolysed immediately to the original quinolizine by water or methanol.

Oxidation of Tetramethyl 4H-*Dibenzo*[ac]*quinolizine*-1,2,3,4-*tetracarboxylate* (II).—(i) The dibenzoquinolizine (7·0 g.) and potassium permanganate (28 g.) were refluxed in acetone (950 ml.) for 1 hr., water (300 ml.) was added, and the acetone removed *in vacuo*. Sulphur dioxide was passed in until reduction of the manganese dioxide was complete and the orange precipitate (3·3 g.) was collected. Acidification of the filtrate gave a cream precipitate (0·6 g.) which was partly inorganic and contained a benzene-crystallisable fraction (A), m. p. 88—90° (265 mg.). The orange precipitate was washed with hot water (3 × 20 ml.); addition of 2N hydrochloric acid to the washings precipitated a white solid (90 mg.) of very similar infrared absorption spectrum to fraction A above. These materials were combined and crystallisation to constant m. p. from benzene gave colourless needles, m. p. 92°, $\lambda_{max.}$ 342, 330, 265, 241, and 235 mμ (characteristic of *N*-alkylated phenanthridones). This material travelled largely as a single *substance* (R_F 0·79; absorbs ultraviolet light; red ferric chloride colour; does not reduce ammoniacal silver nitrate) in solvent A and had R_F 0·92 in solvent B. After drying at 80° its m. p. rose to 118°, and its chromatographic properties remained unchanged (Found: C, 65·5; H, 4·3; OMe, 16·2. $C_{20}H_{15}NO_6$ requires C, 65·7; H, 4·1; 2OMe, 17·0%). It had $\nu_{max.}$ (P) including 3·80 μ (bonded carboxyl-OH), 5·75 and 5·90* (C=O), 6·03 (phenanthridone C=O) and 8·05 μ (ester) and $\lambda_{max.}$ 337 (0·66), 323 (0·86), 300* (0·98), 270* (1·94), 261 (2·36), 253* (1·93), 238 (4·40), 233 (4·43), and $\lambda_{max.}$ after acidification 336 (0·72), 322 (0·84), 310* (0·63), 300* (0·60), 260 (2·35), 250 (2·30), 238 (5·0), and 233 (4·80).

The washed orange precipitate was extracted successively with warm 2N-sodium hydroxide (3 × 10 ml.) and hot 2N-sulphuric acid the insoluble fraction (0·63 g., 23%) was phenanthridone (infrared spectrum; m. p. and mixed m. p. 284°). Acidification of the sodium hydroxide solution gave a precipitate from which was isolated a small quantity of the acid (VI), m. p. 207° (decomp.) (Found: C, 63·3; H, 3·8%), described in detail for expt. (ii).

(ii) The dibenzoquinolizine (II) (10·0 g.) was refluxed in acetone (400 ml.) with potassium permanganate (5·75 g.) for 1 hr.; then more permanganate (11·50 g.) was added and refluxing continued for 1 hr. Water (150 ml.) was added, the acetone removed *in vacuo*, sulphur dioxide passed in, and the insoluble red material (7·7 g.) collected. Apart from an inorganic residue (0·83 g.) this dissolved in chloroform (100 ml.) which slowly deposited phenanthridone (20 mg.). The remaining chloroform solution was passed down a silica gel column (500 g.; British Drug Houses; 30 cm. long, made up in benzene) which was then eluted with benzene (4 l.), and benzene containing chloroform (5%, 2 l.; 20%, 2 l.; 50%, 1·5 l.). Evaporation of these gave almost no residue but elution with pure chloroform (7 l.) gave unoxidised dibenzoquinolizine (5·72 g.). Subsequent elution by methanol (2 l.) and evaporation gave first a red-brown solid B (1·45 g.), m. p. 204° (decomp.), then a colourless solid C (45 mg.), m. p. 252° (decomp.), of very similar infrared absorption spectrum. Solid C gave a purple precipitate with ferric chloride and had $\nu_{max.}$ (P) including 2·90 (hydrate?), 5·81 and 5·96* (C=O), 6·02 (phenanthridone C=O), and 8·04 μ (ester)which are consistent with the compound's being methyl α-(5,6-dihydro-6-oxophenanthridin-5-yl)-α-oxalylacetate (VII); attempts at purification caused decomposition.

Most of solid B dissolved in 2N-sodium hydroxide (20 ml.); after filtration the solution was just acidified by 2N-hydrochloric acid. The cream precipitate (1·02 g.), after four crystallisations from benzene, gave 3-(5,6-*dihydro*-6-*oxophenanthridin*-5-*yl*)-3-*methoxycarbonylpyruvic acid* (VI) as a microcrystalline powder, m. p. 210° (decomp., variable and depressed by traces of moisture) after drying at 100° at 1 mm. (Found: C, 63·8; H, 4·0; N, 4·6; OMe, 9·2. $C_{18}H_{13}NO_6$ requires C, 63·7; H, 3·8; N, 4·1; OMe, 9·1%). It travelled as a single compound (R_F 0·29 and 0·84 in solvents A and B, respectively), appeared dark under ultraviolet light, gave a red ferric chloride colour, and had $\nu_{max.}$ (P) including 2·80w (carboxyl-OH), 3·90m (broad peak, bonded carboxyl-OH), 5·75 and 5·92* (C=O), 6·03 (phenanthridone C=O), and 8·04 (ester). The acid (VI) with ethereal diazomethane gave a product which separated from light petroleum ether, then having m. p. 244° (decomp.). Its infrared absorption spectrum (P) was identical (38 maxima and corresponding minima) in the 2·5—15 μ region with that of solid C mentioned above. It did not absorb at *ca.* 3·90, indicating that esterification had occurred. Attempts at purification caused decomposition.

Methyl 5,6-*Dihydro*-6-*oxophenanthridin*-5-*ylacetate* (V).—(i) Phenanthridone (1·95 g.), sodium hydride (0·3 g.), and sodium-dried xylene (15 ml.) were vigorously stirred at 100° (oil-bath) for 2¼ hr. Methyl bromoacetate (1·53 g.) was added and the conditions were maintained for another 10 hr. Filtration (hot) left a residue from which phenanthridone (1·26 g.) was recovered, and, on cooling, the filtrate yielded *methyl* 5,6-*dihydro*-6-*oxophenanthridin*-5-*ylacetate* (0·77 g.) which separated from 1 : 1 benzene–light petroleum (b. p. 80—100°) in needles, m. p. 161° (Found: C, 72·2; H, 5·0; N, 5·5; OMe, 11·3. $C_{16}H_{13}NO_3$ requires C, 71·9; H, 4·9; N, 5·3; OMe, 11·6%), $\nu_{max.}$ (P) 5·78, 5·95*, 6·07, 6·22, 6·31, 6·37*, 6·40*, 6·48*, 6·62, 6·71, 6·90, and 6·99 μ.

(ii) The keto-acid (VI) (0·1 g.) was refluxed with acetic anhydride (0·2 ml.) for 30 min. and, after cooling, the grey precipitate (44 mg.) was collected. After two crystallisations from benzene–light petroleum (b. p. 80—100°) it had m. p. 161° (Found: C, 72·1; H, 5·1; N, 5·9%), and was identical (mixed m. p., infrared and ultraviolet absorption spectra) with a sample from expt. (i).

(iii) The keto-acid (VI) (101 mg.) was heated for 5 min. at 200°. The residue on crystallisation from methanol gave methyl 5,6-dihydro-6-oxophenanthridin-5-ylacetate, m. p. 161° alone or mixed with a sample from expt. (i).

Dimethyl 2-*Methoxy*-2-2′-*methoxycarbonylethyl*-2,13*b*H-[1,3]-*oxazino*[2,3-f]*phenanthridine*-3,4-*dicarboxylate* (XIII).—The white adduct (X) (0·5 g.) in methanol (100 ml.) was shaken under hydrogen (4 atm.) at room temperature for 4·5 hr. Filtration and evaporation gave pale yellow sticky crystals which dissolved in ether (20 ml.), and this solution was extracted with 2N-hydrochloric acid (10 ml.; then 3 × 5 ml.). Addition of saturated aqueous picric acid to the hydrochloric acid extract gave a bright yellow-orange precipitate of 5,6-dihydrophenanthridine picrate (155 mg., 24%), m. p. 116—118°; this was oxidised on crystallisation from ethanol, yielding phenanthridine picrate, m. p. and mixed m. p. 239°; the infrared absorption spectra (P) of the two specimens were identical.

Evaporation of the dried ($MgSO_4$) ether layer gave a pale yellow oil which solidified (0·36 g.), and two crystallisations from aqueous methanol gave the *tetrahydro-compound* (XIII) as colourless prisms, m. p. 145° (Found: C, 64·1; H, 5·4; N, 3·1; OMe, 26·1. $C_{25}H_{25}NO_8$ requires C, 64·2; H, 5·4; N, 3·0; 4OMe, 26·5%), $\nu_{max.}$ (P) 5·77, 5·81, 6·23, 6·39, 6·69, 6·87, 6·96, and 6·98* μ.

2-Bromo-5-(4,4,5,5-tetrabromo-1,2,5-trimethoxycarbonyl-3-oxopent-1-enyl)phenanthridinium Bromide (XV).—Bromine (0·5 g.) in chloroform (2 ml.) was added to the white adduct (X) (0·4 g.) in chloroform (8 ml.) and after 5 days at room temperature the *pentabromo-bromide* (XV) (0·35 g.) which had separated as yellow needles, m. p. 149° (decomp.), was collected and directly analysed (Found: C, 32·4; H, 2·05; N, 1·90; Br, 52·7; OMe, 9·6. $C_{24}H_{17}Br_6NO_7$ requires C, 31·6; H, 1·90; N, 1·5; Br, 52·7; 3OMe, 9·8%); it had $\nu_{max.}$ (P) 5·76, 5·90, 6·18, 6·28, 6·38, 6·59, 6·67, 6·88, and 6·98* μ. Attempts at purification caused decomposition, and crystallisation from dioxan gave 2-bromophenanthridine hydrobromide, m. p. 275° (decomp.).

The original experiment was repeated, but instead of the bromo-compound's being collected the chloroform solution was evaporated and the residue refluxed with dioxan for 2 hr. After evaporation to dryness the residue was shaken with ether and 2N-hydrochloric acid; basification of the aqueous layer from which the dissolved ether had been vaporised gave a brown precipitate (0·1 g.). Crystallisation from aqueous methanol to constant m. p. gave almost pure 2-bromophenanthridine as colourless needles, m. p. 155° (Found: C, 60·4; H, 3·25; Br, 29·5. Calc. for $C_{13}H_8BrN$: C, 60·5; H, 3·1; Br, 31·0%). It had mixed m. p. 157—159° with authentic 2-bromophenanthridine of m. p. 161° prepared as described before.[15] The infrared absorption spectra (P) of the two specimens were identical in the 2·5—15 μ (33 maxima) region.

Dimethyl 2-(2-Methoxycarbonyl-2-oxoethylidene)-2,13bH-[1,3]-oxazino[2,3-f]phenanthridine-3,4-dicarboxylate (XIV).—The white adduct (X) (0·13 g.) in hot methanol (70 ml.) was treated with a 1% solution of perchloric acid (60% aqueous originally) in methanol (5 ml., 1·25 moles). After several minutes the mixture was concentrated *in vacuo* to 15 ml., and after 12 hr. at −15° a yellow solid (80 mg.) separated. Crystallisation from methanol gave the *ester* (XIV) as yellow hexagons, m. p. 191—192° (Found: C, 63·9; H, 4·3; N, 3·5; Cl, 0·0; OMe, 21·0. $C_{24}H_{19}NO_8$ requires C, 64·15; H, 4·2; N, 3·1; 3OMe, 20·7%), $\nu_{max.}$ (P) 5·74, 6·00, 6·24, 6·58, 6·77, and 6·89 μ. Little conversion took place when the reaction was carried out at room temperature for 17 hr.

Oxidations of the White Adduct (X).—(i) The adduct (1·0 g.) was refluxed with potassium permanganate (6·0 g.) in acetone (200 ml.) for 1 hr. and the mixture worked up as in the oxidation of the "labile" adduct. No compounds were detected in the distillate. The precipitate (0·71 g.), obtained with sulphur dioxide, was extracted with cold 2N-sodium hydroxide (total 6 ml.), and the residue (0·27 g.) was further extracted with concentrated hydrochloric acid followed by more sodium hydroxide. The insoluble material (0·24 g.), after crystallisation from ethanol, gave phenanthridone (66 mg.), m. p. and mixed m. p. 283—284° [correct infrared spectrum (P)].

Acidification of the first sodium hydroxide extract with concentrated hydrochloric acid (1·1 ml.) gave an immediate cream precipitate (10 mg.; m. p. 153—158°; bright orange ferric chloride colour); from the filtrate fraction A [14 mg.; m. p. 198—204° (decomp.)] and subsequently fraction B (trace; m. p. 90—130°) separated. Paper chromatography showed that all fractions were complex mixtures. Fractions A and B contained a compound which had the same R_F (0·30) in solvent A, appearance under ultraviolet light, and ferric chloride colour as the keto-acid (VI). Fraction B contained a larger proportion of this material and, on paper electrophoresis at 7 kv and 60 mA in a Locarte apparatus in pyridine (10 ml.), acetic acid (30 ml.), and water (1 l.), was shown to contain a compound which moved 18·6 cm. towards the anode in 1 hr. and was indistinguishable as regards appearance under ultraviolet light, ferric chloride colour, and movement from the keto-acid (VI) under these conditions. Fraction B also contained a substance which moved the same distance (13·3 cm.) and had the same appearance and ferric chloride colour on the paper as the unidentified substance obtained in expt. (i) in the oxidation of the "stable" adduct (II), but this substance was not clearly resolved on the paper chromatograms.

(ii) The white adduct (X) (0·36 g.), potassium ferricyanide (1·25 g.), and 5% aqueous potassium hydroxide (10 ml.) were refluxed for 16 hr. The white sublimate (7 mg.), m. p. 100°, recovered from the condenser was identified as crude phenanthridine by means of its infrared absorption spectrum. Acidification of the filtered reaction mixture gave a brown precipitate (40 mg.). Chromatography showed that this contained at least 7 compounds and none of the acids mentioned in the Table of ultraviolet absorption spectra could be detected.

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