Heterocyclic Compounds with Bridgehead Nitrogen Atoms. Part IV.[1,2] Cyclopenta[*ij*]pyrido[2,1,6-*de*]quinolizines (Cyclopenta[*cd*]cycl[3,3,3]-azines)

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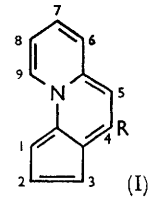
Cyclopenta[*c*]quinolizines react with αβ-acetylenic esters to give cyclopenta[*ij*]pyrido[2,1,6-*de*]quinolizines (cyclopenta[*cd*]cycl[3,3,3]azines). The ^{1}H n.m.r. spectra of the latter show evidence of aromatic character. Protonation of a dimethylcyclopentacyclazine occurred at the 1-position and treatment with benzoyl chloride gave a 1-benzoyl derivative. Other electrophilic reagents caused decomposition.

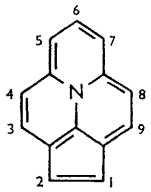
In Part III [1] we described a convenient synthesis of cyclopenta[*c*]quinolizines (I) and showed that this new ring system is highly reactive towards electrophiles at the 1- and 3-positions. We now report [2] that compounds of this class react with αβ-acetylenic esters to yield derivatives (II) of the long-sought [3] pyrido-[2,1,6-*de*]quinolizine (III), otherwise known [4] as cycl-[3,3,3]azine.

4-Methylcyclopenta[*c*]quinolizine (Ia) reacted with dimethyl acetylenedicarboxylate, in benzene at room



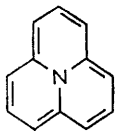
(I)

a : R = Me
b : R = Ph

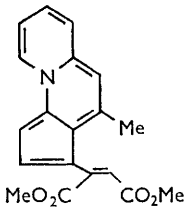


(II)

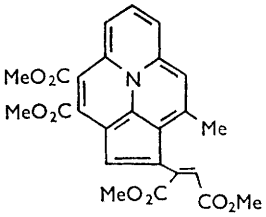
a: 9-Me-3,4-diCO_2Me
b: 9-Me-4-CO_2Et
c: 3,9-diMe-4-CO_2Et
d: 9-Ph-4-CO_2Et
e: 3,9-diPh-4-CO_2Me
f: 9-Me-3-Ph-4-CO_2Me
g: 3-Me-9-Ph-4-CO_2Et
h: 3-Me
i: 3,9-diMe
j: 3-Ph
k: 3,9-diPh
l: 3-Me-9-Ph
m: 1-Bz-3,9-diMe



(III)



(IV)



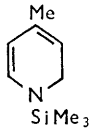
(V)

$R^1 \cdot C \equiv C \cdot COR^2$

(VI)

a : R^1 = H, R^2 = Et
b : R^1 = Me, R^2 = Et
c : R^1 = Ph, R^2 = Me

(VII)



(VIII)

temperature, to give two major products, one orange and one green. The orange compound was a true 1 : 1 adduct; its ^{1}H n.m.r. spectrum showed signals due to one *C*-methyl and two *O*-methyl groups, and eight other protons including one α-pyridine proton (9-position of cyclopenta[*c*]quinolizine) at τ 1·37 (doublet with further splitting) and one olefinic proton at τ 4·27 (sharp singlet). The green compound, on the other hand, was not a true adduct; elemental analysis showed that it contained a slightly lower proportion of hydrogen than the orange compound and its n.m.r. spectrum showed only six protons in addition to those of the methyl groups. In particular, the signals due to the α-pyridine and olefinic protons were absent and, accordingly, the green compound was tentatively formulated as the cyclopenta[*cd*]cycl[3,3,3]azine (IIa).

It seemed probable that the orange compound was a cyclopenta[*c*]quinolizine containing a maleic ester side-chain at the 1- or the 3-position; the *cis*-configuration was assigned on the basis of a comparison of the chemical shift of the olefinic proton with those of the corresponding protons in dimethyl maleate (τ 3·86) [5] and dimethyl fumarate (τ 3·33).[5] That the side-chain was, in fact, in the 3-position [structure (IV)] was shown by the reaction of the orange compound with more dimethyl acetylenedicarboxylate, in boiling nitrobenzene, to give the green cyclopentacyclazine (V), which showed a one-proton olefinic singlet at τ 4·08. The possibility that the orange compound was the 1-substituted isomer of (IV), and that compound (V) had arisen from it by cyclodehydrogenation [to (IIa)] followed by reaction with the acetylenic ester, was eliminated by showing that, in boiling nitrobenzene, the orange compound did not yield the green compound (IIa) and the latter did not react with dimethyl acetylenedicarboxylate.

In seeking conclusive evidence for the formation of the cyclopentacyclazine ring system, we studied the reactions of the cyclopenta[*c*]quinolizines (Ia) and (Ib) with the acetylenic monoesters (VIa, b, and c). The desired green esters (IIb—g) were obtained in yields of 30—55% by conducting the reactions in boiling nitrobenzene, which presumably functions as a dehydrogenating agent. No other media were found to be effective, even in the presence of palladium–charcoal.

[1] Part III, W. K. Gibson and D. Leaver, *J. Chem. Soc.* (*C*), 1966, 324.
[2] Preliminary communication, W. K. Gibson and D. Leaver, *Chem. Comm.*, 1965, 11.
[3] V. Boekelheide and W. G. Gall, *J. Org. Chem.*, 1954, **19**, 499; H. V. Hansen and E. D. Amstutz, *ibid.*, 1963, **28**, 393; V. Boekelheide, H. Fritz, J. M. Ross, and H. X. Kaempfen, *Tetrahedron*, 1964, **20**, 33; D. Leaver and J. D. R. Vass, *J. Chem. Soc.*, 1965, 1629; G. R. Underwood, *J. Org. Chem.*, 1968, **33**, 1313.
[4] R. J. Windgassen, W. H. Saunders, and V. Boekelheide, *J. Amer. Chem. Soc.*, 1959, **81**, 1459.
[5] L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 1960, 2886.

The alkoxycarbonyl groups of the green esters were readily removed by alkaline hydrolysis followed by vacuum-pyrolysis of the resulting acids. In this way, the ester (IIf), obtained from 4-methylcyclopenta[*c*]quinolizine and methyl phenylpropiolate, and the ester (IIg), obtained from 4-phenylcyclopenta[*c*]quinolizine and ethyl methylpropiolate, yielded the same product (III). This shows that the acetylenic linkage and the 4,5-bond of the cyclopenta[*c*]quinolizine contribute equivalent two-carbon units to the final ring system, thus substantiating the cyclopenta[*cd*]cycl[3,3,3]azine structure.

The ^{1}H n.m.r. data for the cyclopentacyclazines (IIh—k) are listed in Table 1. Owing to an initial difficulty in obtaining the spectra of solutions in deuteriochloroform, carbon disulphide was used as solvent. This difficulty now appears to have been due to contamination of a particular sample of deuteriochloroform with traces of copper. A spectrum of one of the compounds, (IIi), in a different sample of deuteriochloroform, obtained later, suggests that the chemical shifts given in the Table are approximately 0·1—0·15 p.p.m. upfield of the values that would have been obtained by use of deuteriochloroform throughout.

TABLE 1

^{1}H Chemical shifts (τ values) and coupling constants (Hz) for cyclopenta[*ij*]pyrido[2,1,6-*de*]quinolizines

	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7	τ_8	τ_9	$J_{1,2}$	$J_{3,4}$	$J_{5,6}(=J_{6,7})$	$J_{8,9}$
(IIh) *	3·04	3·04	(7·62) ‡	3·73				3·59	2·49		(1)		8·3
(IIi) *	3·04	3·04	(7·61)	3·71	3·34	3·05	3·34	3·71	(7·61)		(0·7)	8·0	(0·7)
(IIi) †	2·88	2·88	(7·53)	3·57	3·22	2·93	3·22	3·57	(7·53)				
(IIj) *	2·95	2·83		3·51				3·57	2·47	4·3			8·7
(IIk) *	2·77	2·77		3·40	3·17	2·96	3·17	3·40				8·4	

* In CS_2. † In $CDCl_3$. ‡ Values in parentheses refer to chemical shifts of methyl protons or to H—Me coupling constants.

The assignments in Table 1 are based on the following interpretation of the spectra.

(i) In the spectrum of the 3,9-dimethyl compound (IIi) the signal due to H-1 and H-2 was a singlet (τ 3·04) which, in contrast to the H-4,8 signal, was not broadened by coupling with the methyl protons. The same singlet was present in the spectrum of the 3-methyl compound (IIh), but in that of the 3,8-diphenyl compound (IIk) it was shifted slightly downfield. This deshielding influence of a phenyl group was further manifest in the spectrum of the 3-phenyl compound (IIj) where H-1 and H-2 gave an AB quartet, the lower-field component of which is attributed to H-2.

(ii) The methyl groups of compounds (IIh) and (IIi) showed splitting due to coupling with the *ortho*-situated protons. This led to the recognition of the H-4 signal of (IIh) and the H-4,8 signal of (IIi) as broad singlets of the expected intensities near τ 3·7. The H-8 signal of the 3-methyl compound (IIh) was slightly downfield of H-4 and formed the upfield part of an AB quartet; a signal at τ 2·49 formed the downfield part of the same quartet and was therefore due to H-9. Corresponding signals, none of which was broadened, were recognisable in the spectra of the phenyl compounds (IIj) and (IIk).

(iii) The spectra of the symmetrically-substituted compounds (IIi) and (IIk) contained AB_2 multiplets, analysis of which gave the chemical shifts and the vicinal coupling constant for H-5, H-6, and H-7.

The following features of their n.m.r. spectra lead us to believe that the cyclopentacyclazines are essentially aromatic in character and that the 1,2-bond forms part of the aromatic system.

(i) The ^{1}H chemical shifts fall within a narrow range (τ 2·5—3·7) which, although upfield of most benzenoid proton signals, is not unusually high for an electron-rich aromatic heterocycle. Each of the individual signals of the six-membered ring protons is situated *ca.* 1—1·5 p.p.m. downfield of its counterpart in the spectra of the 1,2-dihydropyridines (VII) [6] and (VIII).[7] (Although not entirely appropriate because of their monocyclic structures, these compounds provide the most suitable non-aromatic models for which n.m.r. data are available.)

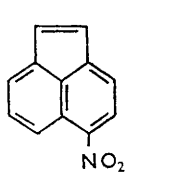
(ii) The methyl protons (τ 7·60 in CS_2) of compounds (IIh) and (IIi) are strongly deshielded relative to those (τ 8·28 in C_6D_6) [7] of the non-aromatic model compound (VIII) and give signals within the chemical shift range normally associated with methyl groups joined to aromatic rings. In accord with the nature of their environment (adjacent to a ring junction) these methyl groups are slightly less shielded than that of 4-picoline (τ 7·71 in CS_2) but more shielded than might have been expected, since the similarly situated methyl group in the cyclopenta[*c*]quinolizine (Ia) gives a signal at τ 7·30 (in $CDCl_3$).

(iii) The vicinal coupling constant ($J_{1,2}$ 4·3 Hz) for the protons of the five-membered ring is only slightly greater than the corresponding value for azulene ($J_{1,2}$ 4·0 Hz) [8a,*] and is considerably less than the value expected for protons joined to a double bond in a five-membered ring (*cf.* cyclopentadiene; $J_{1,2}$ 5·1 Hz).[9] Recent studies [10] have established that, for rings of a

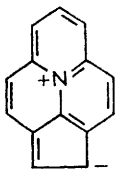
* Most previous authors (including those of ref. 10) have accepted a value of 3·5 Hz [8b] for this coupling constant. However, we believe that the value reported in ref. 8*a* is the result of more accurate and extensive measurements and it is in better accord with our own experience of the n.m.r. spectra of azulenes.

[6] M. Saunders and E. H. Gold, *J. Org. Chem.*, 1962, **27**, 1439.
[7] N. C. Cook and J. E. Lyons, *J. Amer. Chem. Soc.*, 1966, **88**, 3396.
[8] (*a*) D. Meuche, B. B. Molloy, D. H. Reid, and E. Heilbronner, *Helv. Chim. Acta*, 1963, **46**, 2483; (*b*) W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Amer. Chem. Soc.*, 1958, **80**, 3497.
[9] S. L. Manatt and D. D. Elleman, as quoted by J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 3896.
[10] W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Amer. Chem. Soc.*, 1967, **89**, 1438.

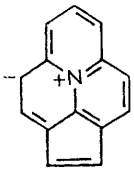
given size, the vicinal coupling constants of protons joined to trigonal carbon atoms show an approximately linear relationship to the π-bond orders of the corresponding carbon–carbon bonds. Thus the 1,2-bond of cyclopenta[*cd*]cycl[3,3,3]azine probably has a π-bond order close to that of the 1,2-bond in azulene; we conclude that it forms part of an aromatic system. To further check this argument, we have measured the coupling constant for the 1- and 2-protons of 5-nitroacenaphthylene [11] (IX), in which the 1,2-bond does not form part of an aromatic system but occupies a stereoelectronic environment otherwise similar to that of the 1,2-bond in the cyclopentacyclazines. The value found ($J_{1,2}$ 5·2 Hz) is in complete accord with the known olefinic character of this bond and supports our conclusion concerning the nature of the 1,2-bond in the cyclopentacyclazines.



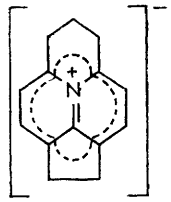
(IX)



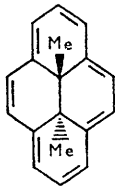
(Xa)



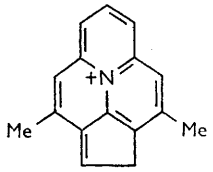
(Xb)



(XI)



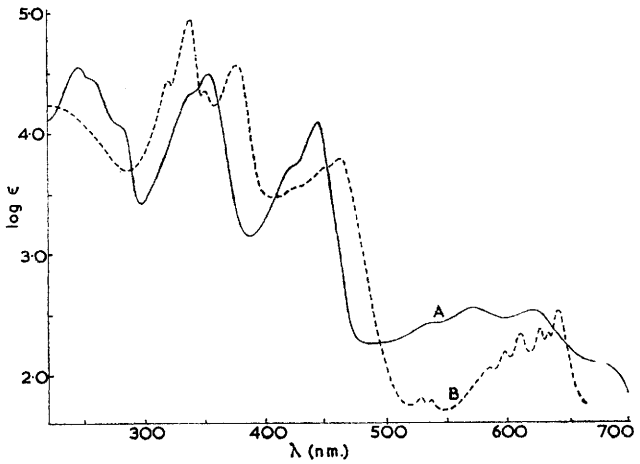
(XII)



(XIII)

If the foregoing conclusions are to be expressed in terms of structural formulae, dipolar structures such as (Xa) and (Xb) must be included as contributors to the resonance hybrid, along with the two equivalent nonpolar structures of type (II). Alternatively, the dipolar contributors may be collectively represented as a structure (XI) in which the 13 peripheral carbon atoms provide the framework for an aromatic system of 14 π-electrons. It is perhaps significant that the electronic spectra of the cyclopentacyclazines show a superficial resemblance (Figure) * to that of the [14]annulene derivative (XII).[12]

The cyclopentacyclazines are highly coloured, crystalline solids, soluble in most organic solvents to give green solutions. They are stable to heat, light, and air but slowly converted into dark amorphous products in the presence of strong acids. A freshly prepared solution of the 3,9-dimethyl compound (IIi), in trifluoroacetic acid, was orange; its n.m.r. spectrum showed a two-proton doublet at τ 6·3 attributable to a CH_2 group coupled (*J ca.* 2 Hz) to one adjacent proton. That this spectrum was due to the 1*H*-cation (XIII) was shown by a study of the position of proton–deuteron exchange: repeated recovery of compound (IIi) from its solution in deuteriotrifluoroacetic acid caused a marked diminution in the intensity of the H-1,2 resonance at τ 2·88 (in $CDCl_3$).



Electronic spectra of (A) compound (IIh) in ethanol and (B) compound (XII) [12] in cyclohexane

Various other reagents (including tetranitromethane, bromine, acetyl chloride, acetic anhydride–stannic chloride, benzoyl chloride, *NN*-dimethylformamide–phosphoryl chloride, and benzenediazonium chloride) were used in attempts to cause electrophilic substitution in compound (IIi). In all except one of these experiments, however, a dark amorphous material was formed and no characterisable product could be isolated. The one successful substitution reaction was a benzoylation, carried out by heating the 3,9-dimethyl compound with benzoyl chloride in the presence of solid sodium hydrogen carbonate. The ^1H n.m.r. spectrum of the benzoyl derivative showed two methyl signals, one of which (at τ 7·2) was shifted 0·4 p.p.m. downfield relative to the other. A deshielding effect of this magnitude must be due to the magnetic anisotropy of the carbonyl group and indicates, therefore, that the benzoyl group is either *ortho-* or *peri-* to one of the methyl groups. The fact that both methyl signals were split (*J ca.* 0·7 Hz), owing to coupling with *ortho*-situated protons (positions 4 and 8), excluded the former possibility and showed that the compound was the 1-benzoyl derivative (IIm).

In attempting to cleave the 1,2-bond or to enlarge the five-membered ring, we studied the reactions of the 3,9-dimethyl compound (IIi) with a number of ' double-bond reagents ' (ozone, osmium tetroxide, periodate–permanganate, chlorocarbene, and ethoxycarbonylcarbene). In each of these reactions, however, the sole product was an amorphous black solid. This suggests that the initial products (possibly cycl[3,3,3]azines) were more reactive than the starting material and had

* In making the extinction coefficient scale logarithmic rather than linear, we have over-emphasised this resemblance.

[11] R. C. Fuson and S. E. Frey, *J. Org. Chem.*, 1954, **19**, 810.
[12] V. Boekelheide and J. B. Phillips, *J. Amer. Chem. Soc.*, 1967, **89**, 1695.

suffered further attack by the reagents [appreciable amounts of compound (IIi) were recovered in some instances].

EXPERIMENTAL

Nuclear magnetic resonance spectra were measured with a Perkin-Elmer R10 (60 MHz) spectrometer, with tetramethylsilane as internal standard and, unless otherwise stated, deuteriochloroform as solvent (0·3—0·4M solutions). Alumina for chromatography was Spence type H and deactivation, where specified, was carried out by treatment [13] with 10% aqueous acetic acid (0·1 ml. per g. alumina). Nitrobenzene was dried over Linde Molecular Sieve (type 4A).

Reaction of 4-*Methylcyclopenta*[c]*quinolizine with Dimethyl Acetylenedicarboxylate*.—Dimethyl acetylenedicarboxylate (1 g.) was added to a solution of the quinolizine (1 g.) in sodium-dried benzene (50 ml.). After 2 hr. at room temperature, the solution was concentrated and chromatographed on deactivated alumina. Elution with benzene–gave (i) a trace of starting material, (ii) a green solid, and (iii) an unidentified red oil. Fraction (ii) gave *dimethyl* 9-*methylcyclopenta*[ij]*pyrido*[2,1,6-de]*quinolizine*-3,4-*dicarboxylate* (0·23 g.) as green needles, m.p. 199—200° (from ethanol) (Found: C, 71·4; H, 4·3; N, 4·5. $C_{19}H_{15}NO_4$ requires C, 71·3; H, 4·7; N, 4·4%). Continued elution with ether gave an orange solid, which gave *dimethyl* 4-*methylcyclopenta*[c]*quinolizin*-3-*ylmaleate* (0·5 g.) as orange plates, m.p. 154—155° [from benzene–light petroleum (b.p. 60—80°)] (Found: C, 70·8; H, 5·3; N, 4·1. $C_{19}H_{17}NO_4$ requires C, 70·9; H, 5·2; N, 3·9%).

The foregoing orange ester (0·4 g.) was treated with more (0·18 g.) dimethyl acetylenedicarboxylate for 1·5 hr. in boiling nitrobenzene. The solvent was evaporated off under reduced pressure and the residue was chromatographed on deactivated alumina. Elution with benzene–ether (9 : 1) yielded a trace of unidentified green solid followed by *dimethyl* 3,4-*bismethoxycarbonyl*-9-*methylcyclopenta*[ij]*pyrido*[2,1,6-de]*quinolizin*-1-*ylmaleate* (0·32 g.) as dark green needles, m.p. 203—204° (from ethanol) (Found: C, 64·7; H, 4·4; N, 3·0. $C_{25}H_{21}NO_8$ requires C, 64·8; H, 4·5; N, 3·0%).

Alkyl Cyclopenta[ij]*pyrido*[2,1,6-de]*quinolizine*-4-*carboxylates* (IIb—g).—4-Methyl- or 4-phenyl-cyclopenta[*c*]-quinolizine was treated with a three-fold excess of the appropriate acetylenic ester (VIa, b, or c) in boiling nitrobenzene (50 ml. per g. quinolizine) for 1·5 hr. The solvent was evaporated off under reduced pressure and the residue was chromatographed, in benzene, on alumina. The material from the initial green fraction was recrystallised from ethanol to yield the required ester (see Table 2).

TABLE 2

Alkyl cyclopenta[*ij*]pyrido[2,1,6-*de*]quinolizine-4-carboxylates

	Yield (%)	M.p.	Found (%) C	H	N	Formula	Reqd. (%) C	H	N
(IIb)	33	114—116°	77·8	5·2	5·3	$C_{18}H_{15}NO_2$	78·0	5·4	5·0
(IIc)	53	98—99	78·4	5·7	4·8	$C_{19}H_{17}NO_2$	78·4	5·8	4·8
(IId)	36	210—211	81·3	5·15	4·0	$C_{23}H_{17}NO_2$	81·4	5·0	4·1
(IIe)	51	195—196	83·5	4·7	3·7	$C_{28}H_{19}NO_2$	83·9	4·7	3·5
(IIf)	54	171—172	81·7	4·9	4·3	$C_{23}H_{17}NO_2$	81·4	5·0	4·1
(IIg)	45	128—129	81·8	5·2	4·1	$C_{24}H_{19}NO_2$	81·6	5·4	4·0

Cyclopenta[ij]*pyrido*[2,1,6-de]*quinolizines* (IIh—l).—The foregoing esters were hydrolysed by heating with an excess of potassium hydroxide in boiling 2-methoxyethanol for 3·5 hr. After evaporation of the solvent under reduced pressure, the residues were each dissolved in the minimum volume of water or aqueous ethanol and the solutions were made slightly acid by careful addition of concentrated hydrochloric acid. The carboxylic acids that precipitated were filtered off, washed with aqueous ethanol, and dried *in vacuo*.

Decarboxylation was best achieved by heating the finely powdered acids (0·1—0·15 g.), intimately mixed with asbestos wool, in an evacuated (<1 mm.) sublimation apparatus until accumulation of green material on the cold finger was complete. The products (Table 3) were recrystallised from ethanol or, in the case of (IIk), from 2-methoxyethanol.

TABLE 3

Cyclopenta[*ij*[pyrido[2,1,6-*de*]quinolizines

	Yield (%) *	M.p.	Found (%) C	H	N	Formula	Reqd. (%) C	H	N
(IIh)	84	102—103°	87·7	5·2	6·8	$C_{15}H_{11}N$	87·8	5·4	6·8
(IIi)	72	125—126	87·6	5·9	6·8	$C_{16}H_{13}N$	87·7	5·9	6·4
(IIj)	83	121—122	89·2	4·7	5·2	$C_{20}H_{13}N$	89·9	4·9	5·2
(IIk)	82	186—187	90·85	5·1	4·3	$C_{26}H_{17}N$	91·0	5·0	4·1
(III)	90, 78 †	127—128	89·6	5·5	5·2	$C_{21}H_{15}N$	89·7	5·3	5·0

* From the ester. † Yields from (IIf) and (IIg) respectively; the products from these two sources were shown to be identical by mixed m.p. and by comparison of their i.r. spectra.

TABLE 4

U.v. and visible spectra of cyclopenta[*ij*]pyrido[2,1,6-*de*]quinolizines (λ in nm.)

	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε
(IIa)	232	4·32	334	4·15	441	4·11	615	2·7
	268	4·44	378	4·21				
	304	4·29						
(IIb)	(235)	4·31	335	4·23	414	3·97	(518)	2·41
	255	4·44	384	4·11	437	4·40	552	2·56
	306	4·31					598	2·54
							652	2·20
(IId)	279	4·69	349	4·29	425	4·01	(540)	2·38
	(308)	4·30	(369)	4·23	447	4·41	572	2·49
			393	4·17			622	2·46
(IIh)	246	4·55	(341)	4·34	425	3·72	(537)	2·40
	(254)	4·48	353	4·49	444	4·08	571	2·54
	(282)	4·06					620	2·52
							681	2·06
(IIj)	255	4·55	(339)	4·13	436	3·68	(559)	2·40
	277	4·61	363	4·32	449	4·02	599	2·56
							650	2·59
							719	2·27
(IIm)	248	4·02	343	4·09	451	3·73	525	3·42
			368	3·71			567	3·40
							612	3·23

Values in parentheses refer to shoulders or inflections.

Deuteriation of 3,9-*Dimethylcyclopenta*[ij]*pyrido*[2,1,6-de]-*quinolizine*.—The dimethyl compound (0·06 g.) was dissolved in deuteriotrifluoroacetic acid (0·5 ml.) at room temperature. After 4 min., the solution was diluted with deuterium oxide (1·5 ml.) and neutralised with anhydrous potassium carbonate to liberate the cyclazine. The latter was extracted into benzene (2 × 10 ml.) and the extract was dried ($MgSO_4$) and evaporated. The residue was

[13] K. R. Farrar, J. C. Hamlet, H. B. Henbest, and E. R. H. Jones, *J. Chem. Soc.*, 1952, 2665.

subjected to a further two cycles of the foregoing operations and the final residue was chromatographed on alumina to yield the deuteriated cyclazine (0·04 g.).

This product gave a ^{1}H n.m.r. spectrum (in $CDCl_3$) in which the peak at τ 2·88 (H-1,2) was *ca.* one fifth as intense as the corresponding peak in the spectrum of the parent compound. The peak at τ 3·57 (H-4,8) appeared to have suffered a slight decrease in intensity but the intensities of the remaining peaks were unchanged.

1-*Benzoyl*-3,9-*dimethylcyclopenta*[ij]*pyrido*[2,1,6-de]*quinolizine*.—The 3,9-dimethyl compound (0·2 g.) was boiled for 3 min. with benzoyl chloride (6 ml.) containing sodium hydrogen carbonate (0·1 g.) and the solution was then shaken with an excess of 2M-aqueous sodium hydroxide until no benzoyl chloride remained. Extraction with chloroform yielded a tarry material which was chromatographed on alumina, in benzene, to yield the *benzoyl compound* (0·18 g.) as brown crystals, m.p. 203—205° (from ethanol) (Found: C, 85·1; H, 5·3; N, 4·3. $C_{23}H_{17}NO$ requires C, 85·4; H, 5·3; N, 4·3%).

U.v. and Visible Spectra.—The spectra were measured with a Perkin-Elmer 137-UV spectrophotometer. Data for ethanol solutions of a representative selection of compounds are listed in Table 4.

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