# The Photocyclisation of 1,2-Diarylpyridinium Cations and the Photobiscyclisation of 1,2,6-Triarylpyridinium Cations [1]

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Photocyclisation of 1-(2-pyridyl)-2-arylpyridiniums yields benzo[c]pyrido[1,2-a]-1,8-naphthyridinylinium cations. Photobiscyclisation of 1,2,6-triarylpyridiniums gives benzo[8,9]quinolizino[4,5,6,7-fed]phenanthridinylium cations and their 9-aza-derivatives. Electron donor substituents tend to lower the yields which are otherwise high. The structures are supported by X-ray crystallographic analysis and by ultraviolet and n.m.r. spectra.

IN the course of investigations in connection with polyarylpyridines as leaving groups,[2] our attention was attracted to the polyarylpyridinium betaines of type (1)

(1)
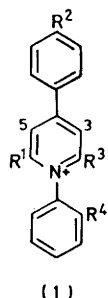
	R[1]	R[2]	R[3]	R[4]
a;	Ph	H	Ph	CO_2^-
b;	p—Tol	H	Ph	CO_2^-
c;	Ph	H	Me	CO_2^-
d;	Ph	H	Ph	Me
e;	Ph	H	Ph	OH
f;	Ph	H	Ph	CO_2H
g;	p—Tol	H	Ph	CO_2H
h;	Ph	H	Me	CO_2H

(2)
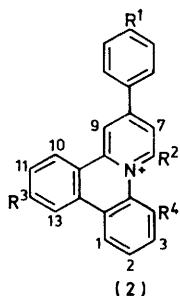
	R[1]	R[2]	R[3]	R[4]
a;	H	Ph	H	CO_2^-
b;	H	Ph	Me	CO_2^-
c;	H	p—Tol	H	CO_2^-

(3)

(4)

as a potential source of benzyne *via* a photochemical decarboxylative elimination analogous to that observed with benzenediazonium-2-carboxylate.[3] Photolysis of this betaine led, however, not to benzyne, but to a

photoelectrocyclisation. This result led us to a more thorough investigation of the photochemistry of polyarylpyridinium betaines and related pyridinium salts, some of the results of which are reported in this paper.

Photochemical cyclisations of polyphenyls to condensed benzenoid derivatives are well-documented,[4] and the configurational restraints in the model stilbene system, (3)→(4), have recently been reported.[5] In the heterocyclic field, similar cyclisations have been found in xanthylium and acridinium salts [6] and later for pyridone analogues of stilbene.[7] Recently, Dorofeenko and his co-workers [8] reported the photocyclisation of 1,2-diphenylpyridinium salts, *e.g.* (5a), to fused tetracyclic derivatives (6a). In the course of our investigation we have independently confirmed the cyclisation (5a)→(6a), but under our conditions [9] the 1,2,6-triphenyl derivative (5c) underwent a double cyclisation to give the fused hexacycle (7a), a derivative of the previously unknown benzo[8,9]quinolizino[4,5,6,7-fed]phenanthridinylium ring system.† The present paper is concerned with the extension of this reaction to other polyarylpyridinium salts and betaines of this type, as well as a brief consideration of the mechanism of the photocyclisation and the factors affecting the outcome of the reaction.

RESULTS AND DISCUSSION

Preparation of Pyridinium Salts and Betaines.—The pyridinium salts (Tables 1, 2) were in general prepared using standard procedures by reaction of the corresponding polyarylpyrylium salts with anilines or aminoheterocycles. Use of carboxy-substituted anilines, followed by treatment of the product with base led to the appropriate betaines (Table 3), as shown by the disappearance of carbonyl and perchlorate bands in the i.r. spectrum at 1 720 and 1 080 cm^{-1} respectively. Most of the betaines (and many of the polycyclic photoreaction products) crystallise with small variable amounts of water of crystallisation; this is difficult to remove and is not readily amenable to accurate determination using, *e.g.*, the Karl-Fischer reagent, but shows in the i.r. spectrum. Low yields were obtained in some pyridin-

† In unpublished work with Dr. El-Shafie we have shown that under different conditions the intermediate product (6c) of monocyclisation can be isolated.
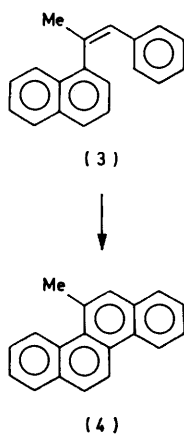
ium salt preparations in EtOH due to a side-reaction involving hydrolysis to pyrylium salt pseudo-base, and in these cases the use [10] of anhydrous HCONMe$_2$ as solvent for the reaction may be preferable. The physical properties of pyridinium salts and betaines prepared in this manner are given in Table 3. The pyridinium

methanol at 300 nm has led to the same product in similar yield. However, the corresponding 1-(o-substituted phenyl)-2-methylbetaine (1c) failed to cyclise: for this compound models indicate considerable steric interaction in the transition state as well as in the product (see below).

TABLE 1

Preparation of pyridinium perchlorates

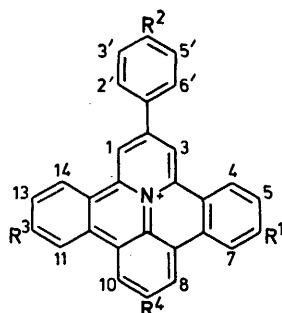| | Starting materials | | Pyridinium cation substituents | | | | | | Recrystallisation | | |
No.	Amine	Pyrylium salt	1	2	4	6	Time	Solvent	Yield (%)	M.p. (°C)	Crystal form
(1d)	o-Toluidine	(16b)	o-Tol	Ph	Ph	Ph	3 h	MeOH	92	262 [a]	Prisms
(1e)	2-Aminophenol	(16b)	2-Hydroxyphenyl	Ph	Ph	Ph	5 h	EtOH	83	253 [b]	Brown prisms
(1f)	Anthranilic acid	(16b)	2-Carboxyphenyl	Ph	Ph	Ph	4 days	2-PrOH	70	273—275 [c]	Prisms
(1g)	Anthranilic acid	(16c)	2-Carboxyphenyl	Ph	Ph	p-Tol	4 days	EtOH–EtOAc	42.5	246	Needles
(1h)	Anthranilic acid	(16a)	2-Carboxyphenyl	Ph	Ph	Me	4 days	2-PrOH	76	177—179	Needles
(5a)	Aniline	(16a)	Ph	Ph	Ph	Me	3 h	MeOH	96	224 [d]	Prisms
(5b)	p-Toluidine	(16a)	p-Tol	Ph	Ph	Me	4 h	MeCN–EtOH	93	230—233	Prisms
(5c)	Aniline	(16b)	Ph	Ph	Ph	Ph	3 h	Me$_2$CO–EtOH	88	263 [e]	Prisms
(5d)	p-Toluidine	(16b)	p-Tol	Ph	Ph	Ph	3 h	MeOH	81	237—239 [f]	Prisms
(5e)	Aniline	(16d)	Ph	Ph	p-Tol	Ph	3 h	MeOH	90	300—301	Prisms
(5f)	Aniline	(16e)	Ph	p-Tol	p-Tol	p-Tol	3 h	EtOH	90	242—244	Prisms
(5g)	Aniline	(16c)	Ph	Ph	Ph	p-Tol	1 h	MeCN–Et$_2$O	89	230	Prisms
(5k)	4-Aminophenol	(16b)	4-Hydroxyphenyl	Ph	Ph	Ph	2 h [g]	2-PrOH	95	254—256 [h]	Prisms
(5l)	4-Aminobenzoic acid	(16b)	4-Carboxyphenyl	Ph	Ph	Ph	4 days	EtOH	95.6	318—320	Prisms
(5m)	4-Aminobenzoic acid	(16c)	4-Carboxyphenyl	Ph	Ph	p-Tol	14 h	MeOH	92	180—185	Yellow prisms
(5n)	4-Aminobenzoic acid	(16e)	4-Carboxyphenyl	p-Tol	p-Tol	p-Tol	24 h [i]	2-PrOH	77	205—209	Prisms
(9a)	4-Aminopyridine	(16b)	4-Pyridyl	Ph	Ph	Ph	3 h	MeOH	40.5	250 [j]	Prisms
(9b)	4-Aminopyridine	(16d)	4-Pyridyl	Ph	p-Tol	Ph	3 h	MeOH	47	269—270	Yellow needles
(9c)	4-Aminopyridine	(16e)	4-Pyridyl	p-Tol	p-Tol	p-Tol	3 h	EtOH	51	290—292	Orange prisms
(11a)	2-Aminopyridine	(16a)	2-Pyridyl	Ph	Ph	Me	3 h	Me$_2$CO–EtOH	77	218 [k]	Pale yellow prisms
(11b)	2-Aminopyridine	(16b)	2-Pyridyl	Ph	Ph	Ph	3 h	EtOH	94	262 [l]	Prisms
(11c)	2-Aminopyridine	(16d)	2-Pyridyl	Ph	p-Tol	Ph	3 h	MeOH	97	277—279	Prisms
(11d)	2-Aminopyridine	(16c)	2-Pyridyl	Ph	Ph	p-Tol	3 h	MeOH	87.5	232—234	Needles
(11e)	2-Aminopyridine	(16e)	2-Pyridyl	p-Tol	p-Tol	p-Tol	3 h	EtOH–light petroleum (40—60°)	91	150—152	Prisms
(14)	Aniline	(17)	Ph	Ph	Ph	Ph [m]	3 h	MeCN–Et$_2$O	82 [n]	258—260	Prisms

[a] Lit., m.p. 254—255 °C (W. Dilthey and H. Dierichs, *J. prakt. Chem.*, 1935, **144**, 1; *Chem. Abs.*, 1936, **30**, 460[8]). [b] Lit., m.p. 250—252 °C (unpublished results with J. Lewis). [c] Lit., m.p. 269—272 °C (A. R. Katritzky, A. Krutošíková, C. A. Ramsden, and J. Lewis, *Coll. Czech. Chem. Comm.*, 1978, **43**, 2046). [d] Found: C, 68.6; H, 4.9; N, 3.6. C$_{24}$H$_{20}$ClNO$_4$ requires C, 68.3; H, 4.8; N, 3.3%. [e] Lit., m.p. 260 °C (see footnote a). [f] Lit., m.p. 243—244 °C (see footnote a). [g] Propan-2-ol used as solvent for reaction. [h] Lit.,[18] m.p. 250 °C. [i] n-Pentanol used as solvent for reaction. [j] Lit.,[10] m.p. 230—231 °C. [k] Lit., m.p. 220—222 °C (A. S. Afridi, Ph.D. Thesis, University of East Anglia, 1976, p. 191). [l] Lit., m.p. 300—301 °C (see footnote j). [m] 2′,3-Ethano-. [n] Tetrafluoroborate.

perchlorates show characteristic bands in the i.r. at $\nu_{max.}$ 1 610—1 640 cm^{-1} (C=N) and 1 050—1 100 cm^{-1} (ClO$_4^-$) and in the u.v. at $\lambda_{max.}$ 215—220 (235—255sh) and 300—335 nm [see Supplementary Publication No. SUP 22777 (2 pp.)].*

Photolysis of 1,4,6-Triaryl-2-methylpyridinium Derivatives.—The photocyclisation of (5a) to (6a) in ethanol was reported by Dorofeenko *et al.*[8] Irradiation in

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1979, Index issue.

Photolysis of 2,4,6-Triarylpyridinium Salts and Betaines.—In contrast to the results obtained by the Russian workers using ethanol, the perchlorate of the 1,2,4,6-tetraphenylpyridinium cation (5c) under 300 nm irradiation in methanol readily cyclised to 2-phenylbenzo[8,9]quinolizino[4,5,6,7-*fed*]phenanthridinylium perchlorate (7a) in high yield. The structure of (7a) follows from the complete assignment of its ^{1}H and [13]C n.m.r. spectra and those of the analogous 9-betaines and 9-aza-salts obtained in similar cyclisations of various

(7)

	R^1	R^2	R^3	R^4	Anion
a ;	H	H	H	H	ClO$_4^-$
b ;	H	H	H	Me	ClO$_4^-$
c ;	H	Me	H	H	ClO$_4^-$
d ;	Me	Me	Me	H	ClO$_4^-$
e ;	Me	H	H	H	ClO$_4^-$
f ;	H	H	H	CO$_2^-$	-
g ;	Me	H	H	CO$_2^-$	-
h ;	Me	Me	Me	CO$_2^-$	-
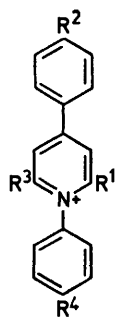
(5)

	R^1	R^2	R^3	R^4
a ;	Me	H	Ph	H
b ;	Me	H	Ph	Me
c ;	Ph	H	Ph	H
d ;	Ph	H	Ph	Me
e ;	Ph	Me	Ph	H
f ;	p–Tol	Me	p–Tol	H
g ;	p–Tol	H	Ph	H
h ;	Ph	H	Ph	CO$_2^-$
i ;	p–Tol	H	Ph	CO$_2^-$
j ;	p–Tol	Me	p–Tol	CO$_2^-$
k ;	Ph	H	Ph	OH
l ;	Ph	H	Ph	CO$_2$H
m ;	p–Tol	H	Ph	CO$_2$H
n ;	p–Tol	Me	p–Tol	CO$_2$H
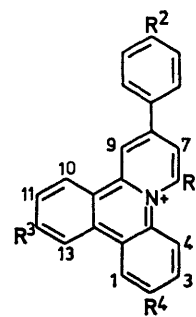
(6)

	R^1	R^2	R^3	R^4
a ;	Me	H	H	H
b ;	Me	H	H	Me
c ;	Ph	H	H	H

related 1-(4-carboxyphenyl)polyarylpyridinium betaines and 1-(4-pyridyl)polyarylpyridinium salts (see below), and has been confirmed by an X-ray crystallographic study.[9]

TABLE 2

Analytical data

| No.	Found (%)			Formula	Required (%)		
	C	H	N		C	H	N
(a) For pyridinium salts							
(1d)	72.7	4.8	2.7	$C_{30}H_{24}ClNO_4$	72.4	4.8	2.8
(1e)	69.3	4.6	2.6	$C_{29}H_{22}ClNO_5$	69.6	4.4	2.8
(1f)	68.0	4.2	2.7	$C_{30}H_{22}ClNO_6$	68.2	4.2	2.6
(1g)	68.5	4.7	2.5	$C_{31}H_{24}ClNO_6$	68.7	4.4	2.6
(1h)	62.4	4.6	3.1	$C_{25}H_{20}ClNO_6$	62.0	4.6	2.9
(5a)	68.6	4.9	3.6	$C_{24}H_{20}ClNO_4$	68.3	4.7	3.3
(5b)	69.0	5.4	2.9	$C_{25}H_{22}ClNO_4$	68.9	5.1	3.2
(5e)	72.5	4.8	2.8	$C_{30}H_{24}ClNO_4$	72.4	4.8	2.8
(5f)	73.2	5.4	2.7	$C_{32}H_{28}ClNO_4$	73.1	5.3	2.7
(5g)	72.3	4.7	2.8	$C_{30}H_{24}ClNO_4$	72.4	4.8	2.8
(5k)	69.6	4.4	2.6	$C_{29}H_{22}ClNO_5$	69.7	4.4	2.8
(5l)	67.6	4.7	2.5	$C_{30}H_{22}ClNO_6$	67.1	4.3	2.6
(5m)	69.5	5.2	2.9	$C_{33}H_{28}ClNO_6$	69.5	4.9	2.5
(5n)	68.2	4.7	2.5	$C_{31}H_{24}ClNO_6$	68.7	4.4	2.6
(9a)	69.4	4.5	5.8	$C_{28}H_{21}ClN_2O_4$	69.4	4.3	5.8
(9b)	70.3	4.6	5.6	$C_{29}H_{23}ClN_2O_4$	70.3	5.1	5.2
(9c)	70.7	5.4	5.0	$C_{31}H_{27}ClN_2O_4$	70.7	5.1	5.3
(11a)	65.2	4.6	6.6	$C_{23}H_{19}ClN_2O_4$	65.3	4.5	6.6
(11b)	69.3	4.6	5.6	$C_{28}H_{21}ClN_2O_4$	69.4	4.3	5.8
(11c)	69.9	4.9	5.4	$C_{29}H_{23}ClN_2O_4$	69.8	4.6	5.6
(11d)	69.8	4.6	5.6	$C_{29}H_{23}ClN_2O_4$	69.8	4.6	5.6
(11e)			5.2	$C_{31}H_{27}ClN_2O_4$			5.3
(14)	74.4	5.0	3.0	$C_{31}H_{24}BF_4N$	74.8	4.8	2.8
(b) For photocyclisation products							
(6a)	68.3	4.6	3.2	$C_{24}H_{18}ClNO_2$	68.7	4.3	3.3
(6b)	69.0	4.6	3.2	$C_{25}H_{20}ClNO_2$	69.2	4.6	3.2
(7a)	72.2	3.6	2.9	$C_{29}H_{18}ClNO_4$	72.5	3.7	2.9
(7b)	73.3	4.1	2.8	$C_{30}H_{20}ClNO_4$	72.9	4.1	2.8
(7c)	72.9	4.5	2.5	$C_{30}H_{20}ClNO_4$	72.9	4.1	2.8
(7d)	72.9	4.6	2.5	$C_{32}H_{24}ClNO_4 \cdot H_2O$	73.2	4.8	2.7
(7e)	72.6	3.9	2.8	$C_{30}H_{20}ClNO_4$	72.9	4.1	2.8
(7f)	78.6	4.6	3.2	$C_{30}H_{17}NO_2 \cdot 2H_2O$	78.4	4.6	3.1
(7g)	79.0	4.7	2.8	$C_{31}H_{18}NO_2 \cdot 2H_2O$	78.8	4.6	3.0
(7h)	79.0	5.2	2.8	$C_{33}H_{23}NO_2 \cdot 2H_2O$	79.0	5.4	2.8
(10a)	69.5	3.9	6.0	$C_{28}H_{17}ClN_2O_4$	69.9	3.5	5.8
(10b)	70.4	4.4	5.4	$C_{29}H_{19}ClN_2O_4$	70.4	3.9	5.7
(10c)	68.9	4.4	5.3	$C_{31}H_{23}ClN_2O_4 \cdot H_2O$	71.2	4.4	5.4
(12a)	65.6	4.4	6.5	$C_{23}H_{17}ClN_2O_4$	65.6	4.1	6.7
(12b)	69.6	4.1	5.9	$C_{28}H_{19}ClN_2O_4$	69.6	3.9	5.8
(12c)	70.1	4.2	5.5	$C_{29}H_{21}ClN_2O_4$	70.1	4.2	5.6
(12d)	67.8	4.2	5.7	$C_{29}H_{19}ClN_2O_4 \cdot H_2O$	67.6	4.5	5.4
(15)	75.4	4.3	2.7	$C_{31}H_{20}BF_4N$	75.5	4.1	2.8

Presumably the reaction occurs in two stages via the intermediate monocyclised product (6c) (but we have been unable to isolate any of this material). The use of various methyl-substituted tetra-arylpyridinium salts

gave the corresponding substituted phenanthridinylium salts in low to fair yields as indicated in Table 4.
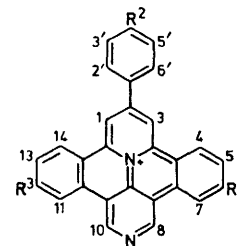
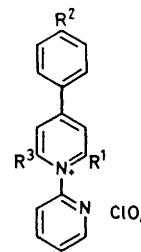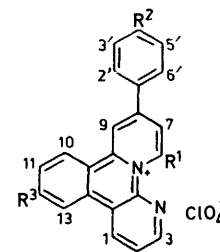It has not proved possible to detect presumed dihydro-

(8)
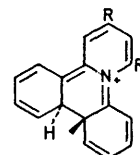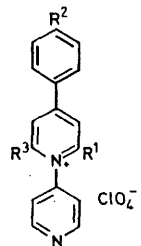
	R^1	R^2	R^3
(9) a;	Ph	H	Ph
b;	Ph	Me	Ph
c;	p-Tol	Me	p-Tol

	R^1	R^2	R^3
(10) a;	H	H	H
b;	H	Me	H
c;	Me	Me	Me

intermediates such as (8), but the occurrence of colour changes on admission of air to the reaction vessel, coupled with the increased yields obtained when the

	R^1	R^2	R^3
(11) a;	Me	H	Ph
b;	Ph	H	Ph
c;	Ph	Me	Ph
d;	Ph	H	p-Tol
e;	p-Tol	Me	p-Tol

	R^1	R^2	R^3
(12) a;	Me	H	H
b;	Ph	H	H
c;	Ph	Me	H
d;	p-Tol	H	H
e;	Ph	H	Me

reaction was carried out in oxygen, argues in favour of such expected intermediates (see below). The existence

TABLE 3

The preparation of betaines from carboxy-2,4,6-trisubstituted pyridinium perchlorates

Pyridinium salt	Betaine	Crystallisation solvent [a]	Yield (%)	M.p. (°C)	Found			Formula	Required		
					C	H	N		C	H	N
(1f)	(1a)	EtOH–Et₂O	93	295—298 [b]	79.3	4.9	3.1	$C_{30}H_{21}NO_2 \cdot 1.5H_2O$	79.5	5.3	3.1
(1g)	(1b)	CHCl₃–EtOAc	91	289	83.1	5.5	3.0	$C_{31}H_{23}NO_2 \cdot 0.25H_2O$	83.5	5.8	3.1
(1h)	(1c)	EtOH–Et₂O	96	223	81.7	5.2	3.8	$C_{25}H_{19}NO_2$	82.2	5.2	3.8
(5l)	(5h)	EtOH	92	328	83.3	4.9	3.6	$C_{30}H_{21}NO_2 \cdot 0.25H_2O$	83.4	5.0	3.2
(5m)	(5i)	EtOH–Et₂O	94	258—260	74.2	5.5	3.1	$C_{31}H_{23}NO_2 \cdot 3.5H_2O$	73.8	5.9	2.8
(5n)	(5j)	EtOH–Et₂O	79	218—222	80.2	5.9	2.8	$C_{33}H_{27}NO_2 \cdot 1.5H_2O$	79.8	6.0	2.8

[a] All the betaines appeared as prisms. [b] Cf. Lit. m.p. of another hydrate 280 °C (Table 1, footnote c).

TABLE 4

Preparative details for photocyclisation and photobiscyclisation products

Starting compound	Irradiation λ	Time (h)	Product No.	R¹	R²	R³	R⁴	Anion	Yield	Solvent	M.p. (°C)[a]	Crystal form
(5a)	300	24	(6a)	Me	H	H	H	ClO_4^-	16	MeOH–MeCN	244[b]	Needles
(5b)	300	72	(6b)	Me	H	H	Me	ClO_4^-	15	MeCN–MeOH	294	Needles
(5c)	300	24	(7a)	H	H	H	H	ClO_4^-	85	MeOH	340	Needles
(5d)	300	24	(7b)	H	H	H	Me	ClO_4^-	36	MeCN	324	Needles
(5e)	300	14	(7c)	H	Me	H	H	ClO_4^-	61	MeOH	298	Needles
(5f)	350	36	(7d)	Me	Me	Me	H	ClO_4^-	12	MeOH	298	Needles
(5g)	300	34	(7e)	Me	H	H	H	ClO_4^-	37	MeCN	320	Needles
(5h)	300	36	(7f)	H	H	H	CO_2^-		10	MeOH	344—345	Prisms
(5i)	300	24	(7g)	Me	H	H	CO_2^-		18	MeOH–MeCN	302	Microprisms
(5j)	350	8	(7h)	Me	Me	Me	CO_2^-		29	HCONMe₂	350	Prisms
(9a)	300	15	(10a)	H	H	H	aza	ClO_4^-	91	MeCN	338	Cubes
(9b)	300	12	(10b)	H	Me	H	aza	ClO_4^-	60	MeOH	269—270	Needles
(9c)	350	24	(10c)	Me	Me	Me	aza	ClO_4^-	8	MeOH	340	Needles
(11a)	300	9	(12a)	Me	H	H		ClO_4^-	38	MeOH	248	Prisms
(11b)	300	24	(12b)	Ph	H	H		ClO_4^-	21	MeOH	290	Prisms
(11c)	300	72	(12c)	Ph	Me	H		ClO_4^-	26.5	MeOH	290	Prisms
(11d)	300	72	(12d)[c]	p-Tol	H	H		ClO_4^-	22	MeCN–Et₂O	279	Prisms
(14)	350	10	(15)	Ph	Ph[d]	H	H	BF_4^-	18	MeCN	326	Prisms

[a] All products melted with decomposition.   [b] Lit.,[22] m.p. 212 °C.   [c] The isomeric 4-aza-2-methyl-6,8-diphenyl compound (12e) was present as a minor contaminant as seen from the ¹H n.m.r. spectrum.   [d] 2′,3-Ethano-.

of an alternative dehydrogenative pathway in non-aerobic conditions involving a second molecule of starting material as hydrogen-acceptor has been envisaged for related reactions.[6a,11]

Starting salts containing in the 1-position a 4-pyridyl group in place of a phenyl group gave the analogous 9-aza-compounds (10a—c) in good yield (Table 4) whilst the 1-(p-carboxyphenyl) betaines (5h, i, j) readily afforded the corresponding 9-phenanthridinylium betaines (7f, g, h) (Table 4).

Photolysis of 2,4,6-Triarylpyridinium Salts without a Free ortho-*Position in the* 1-*Substituent.*—These compounds were expected to undergo a single ring closure only. Thus the analogous 2,4,6-triaryl-1-(2-pyridyl)-pyridinium salts (11a—d) on photolysis, gave by a single cyclisation the benzo[c]pyrido[1,2-a][1,8]naphthyridinylium cations (12a—d), as clearly indicated by the n.m.r. spectra (see below) (Table 5).

Effect of Substituents and the Mechanism of the Reaction.—Comparison of relative yields of the photo-

TABLE 5

¹H N.m.r. spectra (δ) of 8-aryl-dibenzo[c][1,8]naphthyridinylium and -benzo[c]pyrido[1,2-a][1,8]naphthyridinylium perchlorates[a]

Compound no.	(6a)	(6b)	(12a)	(12b)	(12c)	(12d)[b]
R¹(6-)	Me	Me	Me	Ph	Ph	p-Tol
R²(4′-)	H	H	H	H	Me	H
R³(12-)	H	H	H	H	H	H
R⁴(2-)	H	Me	aza	aza	aza	aza
Proton-1	8.8 (dd, J 8 Hz, 2 Hz)	8.6 (d, J 2 Hz)	9.35 (dd, J 8 Hz, 2 Hz)	9.35 (dd, J 8 Hz, 1 Hz)	9.35 (dd, J 8 Hz, 2 Hz)	9.4 (dd, J 8 Hz, 2 Hz)
Proton-2	7.9 (m)	2.6 (s, Me)	8.0 (t, J 8 Hz)	8.1 (m)	8.2 (m)	8.1 (m)
Proton-3	7.9 (m)	7.85 (dd, J 8 Hz, 2 Hz)	8.9 (dd, J 8 Hz, 2 Hz)	7.7 (m)	7.7 (dd, J 8 Hz, 4 Hz)	7.8 (m)
Proton-4	8.8 (dd, J 8 Hz, 2 Hz)	8.75 (dd, J 8 Hz, 2 Hz)				
Proton-6	3.2 (s, Me)	3.2 (s, Me)	3.4 (s, Me)			
Proton-7	8.6 (d, J 2 Hz)	8.6 (d, J 2 Hz)	8.65 (d, J 2 Hz)	8.55 (d, J 2 Hz)	8.5 (d, J 2 Hz)	8.55 (dd, J 2 Hz)
Proton-9	9.4 (d, J 2 Hz)	9.4 (d, J 2 Hz)	9.5 (d, J 2 Hz)	9.6 (d, J 2 Hz)	9.5 (d, J 2 Hz)	9.6 (d, J 2 Hz)
Proton-10	9.2 (dd, J 8 Hz, 2 Hz)	9.15 (dd, J 8 Hz, 2 Hz)	9.3 (dd, J 8 Hz, 2 Hz)	9.25 (dd, J 8 Hz, 2 Hz)	9.25 (dd, J 8 Hz, 2 Hz)	9.25 (dd, J 8 Hz, 2 Hz)
Proton-11	7.9 (m)	7.85 (t, J 8 Hz)	7.95 (m)	8.1 (m)	8.1 (m)	8.1 (m)
Proton-12	7.9 (m)	8.0 (t, J 8 Hz)	8.1 (m)	8.1 (m)	8.1 (m)	8.1 (m)
Proton-13	8.4 (dd, J 8 Hz, 2 Hz)	8.3 (dd, J 8 Hz, 2 Hz)	8.85 (dd, J 8 Hz, 2 Hz)	8.85 (dd, J 8 Hz, 2 Hz)	8.85 (dd, J 8 Hz, 2 Hz)	8.9 (dd, J 8 Hz, 2 Hz)
2′,6′	8.3 (m)	8.3 (m)	8.35 (m)	8.45 (m)	8.35 (d, J 8 Hz)	8.4 (m)
3′,5′	7.7 (m)	7.6 (m)	7.7 (m)	7.45 (m)	7.45 (d, J 8 Hz)	7.45 (m)
4′	7.7 (m)	7.6 (m)	7.7 (m)	7.45 (m)	2.4 (s, Me)	7.45 (m)
R = Ph 2″,3″,4″,5″,6″				7.65 (m)	7.45 (m)	7.7 (m)
R = p-Tol						2.65 (s, Me)

[a] In (CD₃)₂SO.   [b] Spectrum shows the presence of (12e) as a minor component δ 9.5 (d, J 2 Hz, 9-H), 8.7 (s, 13-H), and 2.65 (s, Me).

reaction for a series of substituted compounds shows clearly that electron-donating substituents (but not electron-withdrawing) disfavour the reaction. For example, the yield of product decreases progressively (Table 4) on the successive introduction of methyl substituents into the 1-, 2-, 4-, and 6-aryl rings, whilst with o- or p-hydroxy or o-methyl substituents in the 1-aryl ring, no product was obtained (although the o-methyl group may also exert a strong steric effect, see above).

On the other hand, where the possibility exists [in betaine (1b)] of alternative cyclisations to a phenyl or a p-tolyl group, the latter seems to be preferred judged by the ratio of major to minor product (see Experimental section), but this may reflect other (steric) factors as in the corresponding 1-(2-pyridyl) salt (11d) the situation is reversed.

The reaction with the 1,2,4,6-tetraphenylpyridinium salts is a high yield one for photochemical reaction reflecting the extreme ease, as can be clearly seen from models, of the $4n + 2$ anti-Hückel conrotatory process leading to the presumed trans-dihydro-intermediate (8). [The possibility of a thermally allowed 1,3-prototropic shift to the more stable dihydro-derivative (13) prior to oxidative aromatisation cannot be discounted (cf. ref. 12).] Photocyclisations of this type have been shown [13] to proceed through $\pi-\pi^*$ lowest excited singlet states, and the effect of steric restriction of the conrotative process in this state by the attachment of a 2',3-ethano-bridge in the starting pyridinium salt is well illustrated by the low cyclisation yield obtained with (14).
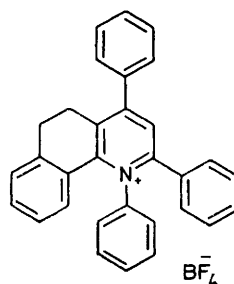
Substitution of the 1-aryl group with electron-withdrawing substituents as in the 4-pyridyl derivatives

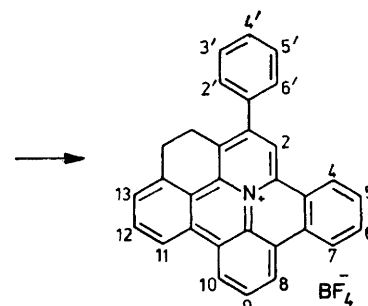pyridine substitution also seemed to cause a marked decrease in yield.

Spectra of Monocyclisation Products.—(a) ¹H *N.m.r. spectra.* The ¹H n.m.r. spectra of the various benzo[c]-pyrido[1,2-a][1,8]naphthyridinylium salts and betaines
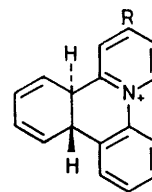
(13)

(14)   (15)

prepared in this work are shown in Table 5. Apart from the general movement to lower field of aromatic protons compared to their position in the spectra of the parent triaryl pyridinium derivatives expected from the increased ring current in the new 14π-annular system, a principal feature of the spectra is the occurrence of two groups of multiple aromatic proton resonances cor-

TABLE 6

U.v. spectral maxima of 8-aryldibenzo[c][1,8]naphthyridinylium and 8-arylbenzo[c]pyrido[1,2-a][1,8]naphthyridin-ylium salts (betaines) in ethanol

No.	Band A λ	Band A log ε	Band B λ	Band B log ε	Band C λ	Band C log ε	Band D λ	Band D log ε	Band E λ	Band E log ε	Band F λ	Band F log	Band G λ	Band G log ε
(6a) [a]	213	4.28	259	4.57	281	4.57		<4.2	332	4.39	360	4.27	396	4.20
(6b)	213	4.36	260	4.48	283	4.56	300	4.38	335	4.31	380	4.19	396	4.25
(6c) [b,c]	215	4.34	243 [d]	4.31	276	4.30	299	4.27	327	4.11	347	4.08	405	3.94
(12a)	215	4.30	250 [e]	4.30	272	4.30		<4.0	322	4.14	374	4.23	392	4.0
(12b)	214	4.34	245	4.41	277	4.42	301	4.26	328	4.24	368	4.23	404	4.14
(12c)	212	4.21	248	4.29	279	4.26	300	4.11	343	4.17	372	4.26	402	4.16
(12d) + (12e)	213	4.16	249	4.29	278	4.32	302	4.19	326	4.17	368	4.14	406	4.06
Mean	214	4.28	251	4.38	278	4.39	300	4.24	330	4.22	367	4.2	400	4.11
Standard deviation	1	0.07	6	0.1	3	0.12	1	0.09	6	0.09	10	0.06	5	0.10

[a] Additional absorbance occurred at λ 230 nm (log ε 4.36).   [b] U.v. data are similar to lit. data (ref. 22).   [c] We thank Dr. El-Shafie for the sample.   [d] Additional absorbance at λ 227 nm (log ε 4.33).   [e] Additional absorbance at λ 233 nm (log ε 4.33).

and the carboxy-betaines is clearly not deleterious. In the 1-(4-pyridyl) series of compounds, the adverse effects of increasing methyl substitution are once more observed. The 1-(2-pyridyl) derivatives, however, in general gave relatively low yields. These general observations are broadly in line with those substituent effects observed by previous workers [14] in the related photocyclisation of stilbenes to phenanthrene derivatives, in which case,

responding to the angular (bay or α-) protons and non-angular (peninsular or β-) protons characteristic for the isosteric triphenylenes.[15] For example, in (2a) these occur at δ 8.8 and 8.0 respectively. Also clearly visible at low field are the 7,9-proton resonances as doublets or in (2a) as a coincidental singlet.

The support for the proposed structures is most clearly demonstrated in the series of 4-aza-derivatives

(10a—c), where the substitution effected considerable simplification. For example in (10c) 1-H appears at low field as a doublet of doublets at δ 9.2, coupled to 2-H (δ 8.1, m) and 3-H, a quartet at δ 7.7. 7-H and 9-H form an AB quartet at δ 8.5, 9.5 whilst 10-H, 13-H (angular) are seen as doublets of doublets at δ 9.35, 8.85 and 1-H, 12-H (non-angular) as a combined multiplet at δ 8.1 as expected.

(b) *Ultraviolet spectra* (*Table* 6). The hexacyclic

has been carried out (Figure) and is in complete agreement with the proposed structure (7a). Particularly prominent at low field are the resonances for C-23 and C-1,5 showing the effect of the adjacent charged nitrogen centre.

(b) *U.v. spectra* (*Table* 8). These compounds show a very characteristic pattern of nine bands (A—I) near 223, 243, 278, 303, 323, 349, 365, 411, and 433 nm. Mean and standard deviations (Table 6) show that the
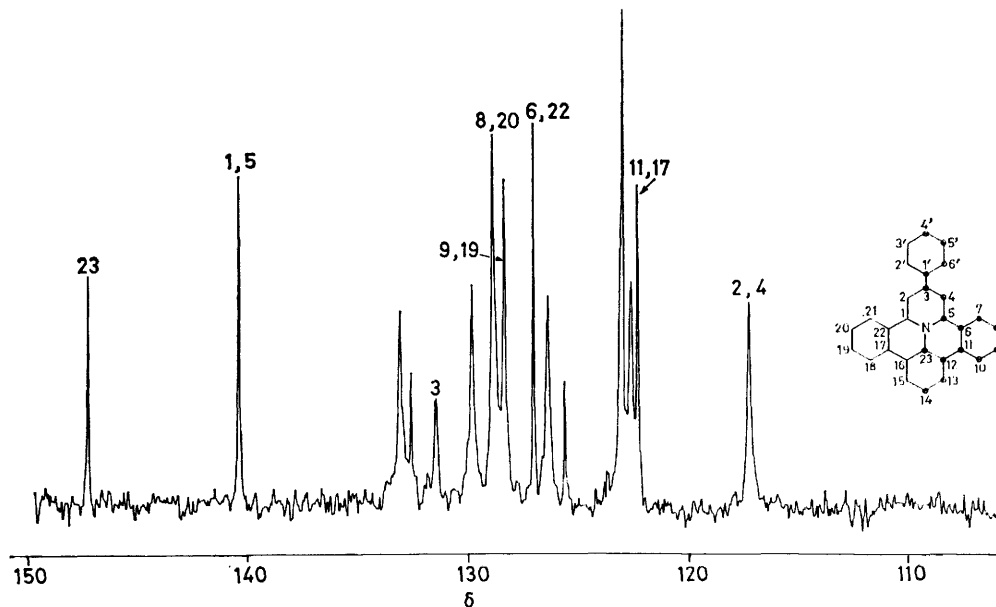
Expanded [13]C n.m.r. spectrum in $(CD_3)_2SO$ of 2-phenylbenzo[8,9]quinolizino[4,5,6,7-*fed*]phenanthridinylium perchlorate (7a)

derivatives display characteristic ultraviolet spectra: a system of seven bands (A—G) of which the wavelengths and extinction coefficients are relatively constant (see Table 6 for means and s.d.): they occur at average values of 213, 249, 278, 301, 330, 363, and 402 nm.

Spectra of 2-Arylbenzo[8,9]quinolizino[4,5,6,7-fed]-phenanthridinylium Salts and Betaines.—(a) [1]H *N.m.r. spectra* (*Table* 7). The most notable effect on the proton spectrum of the double cyclisation is the considerable simplification due to the symmetry (or near symmetry). The 1,3-protons now appear as 2 H singlets at low field, whilst the groups of angular (4, 14-H, 9-H, 7, 11-H) and higher field non-angular (5, 13-H, 6, 12-H) are clearly distinguished. For example, in the 9-aza-trimethyl derivative (7d) where the substitutions affect further simplification, the 1,3-H singlet is at δ 9.0. The angular 4,14-H; 7,11-H show as doublet and broad singlet respectively at δ 8.75, 8.4, the non-angular 5,13-H as a broad doublet at δ 7.45, and the aza-ring protons 8,10-H as an extreme low field singlet at δ 9.8.*

(b) [13]C *N.m.r. spectra.* The proton decoupled [13]C n.m.r. spectrum of compound (7a) showed 16 of the theoretically expected 17 lines. A complete assignment

* The ^{1}H and [13]C n.m.r. spectra of (7a) are significantly altered by the presence of traces of water; some of the present assignments may need modification (unpublished work with Miss B. J. Agha).

effects of substitution on this pattern of frequencies and on the intensities is minor.

EXPERIMENTAL

Melting points were determined with a Reichert apparatus and are uncorrected. Spectra were recorded with the following instruments: i.r., Perkin-Elmer 257; mass, Hitachi-Perkin-Elmer RMU-6E; u.v., Unicam SP800A; n.m.r., R12 Perkin-Elmer and Varian HA-100 and [13]C n.m.r., FX 100 JEOL. In all n.m.r. measurements, tetramethylsilane was used as an internal standard. Irradiations with an external source were performed with a Rayonet reactor (RPQ-100), with 3 500 Å, 3 000 Å, or 2 537 Å lamps in quartz flasks.

Preparation of 2,4,6-Trisubstituted Pyrylium Salts.—2,4,6-Triphenylpyrylium perchlorate (16b),[16] m.p. 280 °C, 2-methyl-4,6-diphenylpyrylium perchlorate (16a),[17] m.p. 274 °C, 2,4-diphenyl-6-*p*-tolylpyrylium perchlorate (16c),[18] m.p. 225 °C, 2,6-diphenyl-4-*p*-tolylpyrylium perchlorate (16d).[18] m.p. 279 °C, and 5, 6-dihydro-2,4-diphenylnaphtho-[1,2-*b*]pyrylium tetrafluoroborate (17),[19,†] m.p. 270—273 °C were prepared by previously described methods.

2,4,6-*Tri-*p-*tolylpyrylium Perchlorate* (16e).—4,4'-Dimethylchalcone [20] (69.15 g, 0.2 mol) and 4-methylacetophenone (21.75 g, 0.16 mol), were heated together at 100 °C for 2 h. The mixture was treated with perchloric acid (73% aq.; 30.25 g, 0.22 mol), stirred vigorously for 2 h, EtOH

† We thank Miss A. Chermprapai for the sample.

(50 ml) was added and the whole heated under reflux for 0.5 h. The solid was separated by filtration, the solution was diluted with Et₂O (360 ml), and the precipitated orange *solid collected*. Recrystallisation of the combined solid product from MeOH–Et₂O (1 : 5) gave the *perchlorate* (16e)

(see Table 1). The precipitated solid was filtered off after cooling, and if necessary addition of ether, and recrystallised from a suitable solvent as indicated. The yields and physical properties of pyridinium salts prepared in this manner are given in Table 1 and the analytical data for

TABLE 7

¹H N.m.r. spectra ^{a} (δ p.p.m.) of 2-arylbenzo[8,9]quinolizino[4,5,6,7-*fed*]phenanthridinylium salts (betaines) (7a—h) and (10a—c)

Anion	Compound	6 R	4' R'	12 R''	9 R'''	1,3	4,14	5,13	6,12	7,11	8,10	9	2',6'	3',5'	4'
ClO₄⁻	(7a)	H	H	H	H	9.05 (s)	8.8 (dd, *J* 8 Hz, 2 Hz)	7.7 (m)	7.7 (m)	8.3 (dd, *J* 8 Hz, 2 Hz)	8.4 (d, *J* 8 Hz)	7.7 (m)	8.2 (m)	7.7 (m)	7.7 (m)
ClO₄⁻	(7b)	H	H	H	Me	9.2 (s)	8.9 (dd, *J* 8 Hz, 2 Hz)	7.85 (m)	7.85 (m)	8.3 (m)	8.3 (m)	2.4 (s, Me)	8.3 (m)	7.85 (m)	7.85 (m)
ClO₄⁻	(7c)	H	Me	H	H	8.9 (s)	8.75 (dd, *J* 8 Hz, 2 Hz)	7.65 (m)	7.65 (m)	8.35 (dd, *J* 8 Hz, 2 Hz)	8.5 (d, *J* 8 Hz)	7.70 (t, *J* 8 Hz)	8.1 (d, *J* 8 Hz)	7.3 (d, *J* 8 Hz)	2.4 (s, Me)
ClO₄⁻	(7d)	Me	Me	Me	H	8.5 (s)	8.35 (d, *J* 8 Hz)	7.3 (dd, *J* 8 Hz, 2 Hz)	2.25 (s, Me)	7.7 (bs)	8.1 (d, *J* 8 Hz)	7.25 (m)	7.9 (d, *J* 8 Hz)	7.2 (d, *J* 8 Hz)	2.4 (s, Me)
ClO₄⁻	(7e)	Me	H	H	H	8.6 (s)	8.4 (m)	7.14 (d, *J* 8 Hz)	7.5 (m)	7.9 (m)	7.9 (m)	6.9 (m)	7.9 (m)	7.5 (m)	7.5 (m)
	(7f) ^{b}	H	H	H	CO₂⁻	8.3 (s) 9.4 (s)	7.5 (m) 8.7 (dd, *J* 8 Hz, 2 Hz)	7.15 (m) 7.8 (m)	2.0 (s, Me) 7.8 (m)	8.6 (dd, *J* 8 Hz, 2 Hz)	9.25 (s)		7.8 (m)	7.6 (m)	7.6 (m)
	(7g) ^{b,c}	Me	H	H	CO₂⁻	9.6 (s)	8.85 (m)	8.1 (m)	8.1 (m, 12-H) 2.8 (s, 6-Me)	8.6 (bs, 7-H) 8.85 (m, 11-H)	9.4 (s)		8.1 (m)	7.8 (m)	7.8 (m)
	(7h) ^{b}	Me	Me	Me	CO₂⁻	9.4 (s)	8.7 (d, *J* 8 Hz)	7.85 (dd, *J* 8 Hz, 1 Hz)	2.7 (s, Me)	8.5 (bs)	9.25 (s)		8.05 (d, *J* 8 Hz)	7.5 (d, 8 Hz)	2.6 (s, Me)
ClO₄⁻	(10a)	H	H	H	aza	9.5 (s)	9.3 (dd, *J* 8 Hz, 1 Hz)	8.1 (t, *J* 8 Hz)	7.9 (t, *J* 8 Hz)	9.0 (dd, *J* 8 Hz, 1 Hz)	10.2 (s)		8.5 (m)	7.7 (m)	7.7 (m)
ClO₄⁻	(10b)	H	Me	H	aza	9.45 (s)	9.2 (dd, *J* 8 Hz, 2 Hz)	8.0 (t, *J* 8 Hz)	7.85 (t, *J* 8 Hz)	8.9 (dd, *J* 8 Hz, 2 Hz)	10.15 (s)		8.3 (d, *J* 8 Hz)	7.4 (d, *J* 8 Hz)	2.45 (s, Me)
ClO₄⁻	(10c)	Me	Me	Me	aza	9.0 (s)	8.75 (d, *J* 8 Hz)	7.45 (dd, *J* 8 Hz, 2 Hz)	2.45 (s, Me) ^{d}	8.4 (bs)	9.8 (s)		8.15 (d, *J* 8 Hz)	7.3 (d, *J* 8 Hz)	2.45 (s, Me) ^{d}
ClO₄⁻	(15) ^{e}	H	H	H	H	8.8 (1 H, s)	8.1 (1 H, m)	7.8 (m)	7.8 (m)	8.6 (m)	8.1 (m)	7.8 (m)	8.1 (m)	7.6 (m)	7.6 (m)

^{a} In (CD₃)₂SO unless otherwise indicated. ^{b} In CF₃CO₂H. ^{c} Additional peaks at δ 9.65 and 9.5 indicate contamination by *ca*. 25% of a similar compound. ^{d} Overlaps with solvent. ^{e} Ethano-group across 3,4-positions—an additional signal occurred at δ 3.2 (4 H, m).

as orange microprisms (21.45 g, 30%), m.p. 310 °C (decomp.) (Found: C, 69.3; H, 5.4. C₂₆H₂₃ClO₄ requires C, 69.3; H, 5.1%); ν$_{max.}$ (Nujol) 1 630 (C=C) and 1 085 (ClO₄) cm⁻¹; δ(CF₃CO₂H) 2.55 (9 H, s), 7.85 (12 H, m), and 8.36 (2 H, s).

Preparation of Pyridinium Salts from 2,4,6-Trisubstituted Pyrylium Salts.—General procedure. A mixture of the appropriate pyrylium salt and amine in absolute EtOH was heated under reflux for 3 h, or, in the case of the carboxy-substituted salts, until the reaction was complete

these and their photocyclisation products are given in Table 2.

Preparation of Betaines from Carboxy-substituted Pyridinium Salts.—2-(2,4,6-Triphenyl-1-pyridinio)benzoate (1a). To a solution of 1-(2-carboxyphenyl)-2,4,6-triphenyl-pyridinium perchlorate (1f) (1 g, 0.001 9 mol) in the minimum of MeOH (25 ml) was added solid KOH (0.2 g, 0.003 mol) until pH 8—9. The reaction mixture was stirred for 25 min and the precipitated potassium perchlorate filtered off. The MeOH filtrate was concentrated to 10 ml *in*

TABLE 8

U.v. spectral maxima ^{a} of 2-arylbenzo[8,9]quinolizino[4,5,6,7-*fed*]phenanthridinylium salts (betaines)

No.	Band A λ	log ε	Band B λ	log ε	Band C λ	log ε	Band D λ	log ε	Band E λ	log ε	Band F λ	log ε	Band G λ	log ε	Band H λ	log ε	Band I λ	log ε
(7a)	228	4.58	240	4.54	278	4.50	302	4.70	326	4.27	349	4.32		<4.3	410	3.82	432	3.90
(7b)	231	4.62	241	4.59	280	4.58	305	4.72	330	4.3	349	4.32	364	4.26	410	3.82	432	3.90
(7c)	228	4.49	242	4.43	279	4.35	300	4.42	316	4.48	350	4.26	366	4.48	408	3.75	430	3.79
(7d)	237	4.57	245	4.59		<4.0	305	4.43	321	4.45		<4.0	364	4.14	412	3.89	436	4.02
(7e)	228	4.51	243	4.53	278	4.42	304	4.66	327	4.25	349	4.28		<4.0	410	3.81	432	3.91
(7f)	214	4.30	243	4.53	280	4.39	304	4.68	332	4.23	350	4.30	364	4.23	416	3.75	439	3.83
(7g)	216	4.30	245	4.53	282	4.39	305	4.67	334	4.23	350	4.28		<4.2	418	3.78	441	3.87
(7h)	220 ^{b}	4.32	254	4.56		<4.1	308	4.57	318	4.55	354	4.32	368	4.29	418	3.78	440	3.96
(10a) ^{c}	215	4.40	235	4.62	275	4.28	300	4.39	310	4.36	350	4.04		<3.9	406	3.6	428	3.65
(10b)	218	4.40	237	4.66	268	4.38	301.5	4.39	317	4.38	348	4.19	366	4.17	406	3.76	428	3.64
(10c)	217 ^{d}	4.05	249	4.35	279sh	4.20	302	4.39	317	4.39	350	4.14	362	4.14	408	3.68	433	3.78
(15)	228	4.50	242	4.43	278	4.39	302	4.59	333	4.13	345	4.07		<3.8	410	3.78	432	3.88
Mean	223	4.42	243	4.53	278	4.39	303	4.55	323	4.34	349	4.23	365	4.24	411	3.76	433	3.8
Standard deviation	8	0.16	5	0.09	4	0.10	2	0.14	7	0.12	2	0.1	2	0.12	4	0.07	4	0.11

^{a} In EtOH unless otherwise indicated. ^{b} Additional band appeared at λ 234 nm (log ε 4.43). ^{c} In MeOH. ^{d} Additional band appeared at λ 232 nm (log ε 4.35).

vacuo, then Et$_2$O (100 ml) was added and the whole cooled at 0 °C overnight. The separated *betaine* was collected and recrystallised from EtOH–Et$_2$O to give colourless prisms (0.8 g, 93%), m.p. 295—298 °C (decomp.).

Other betaines similarly prepared are listed in Table 3.

Photolysis of Betaines and Pyridinium Salts.—General *procedure.* The betaine or pyridinium salt dissolved in MeOH was stirred in a quartz photolytic vessel equipped with an oxygen bubbler and irradiated at 254, 300, or 350 nm using a Rayonet reactor.[21] When the irradiation was complete the solid product was filtered off, the filtrate
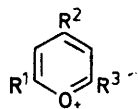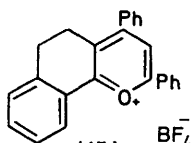
	R^1	R^2	R^3
a ;·	Ph	Ph	Me
b ;	Ph	Ph	Ph
c ;	Ph	Ph	*p*-Tol
d ;	Ph	*p*-Tol	Ph
e ;	*p*-Tol	*p*-Tol	*p*-Tol

concentrated *in vacuo* to give a second crop, and the combined solids recrystallised from a suitable solvent.

2-Methyl-1,4,6-triphenylpyridinium Perchlorate.—The salt (0.5 g) in MeOH (150 ml) was photolysed at 300 nm for 24 h as described above. The solid obtained was recrystallised from MeCN–MeOH to give 6-methyl-8-phenylbenzo[*c*]-pyrido[1,2-*a*][1,8]naphthyridinylium perchlorate (6a) as yellow needles (0.08 g, 16%), m.p. 244 °C (decomp.) [lit.,[22] m.p. 212 °C (decomp.)] (Found: C, 68.3; H, 4.6; N, 3.2. Calc. for C$_{24}$H$_{18}$ClNO$_4$: C, 68.7; H, 4.3; N, 3.3%); $v_{max.}$ (CHBr$_3$) 1 620s, 1 600s, 1 590m, 1 530m, 1 485w, 1 455s, 1 440s, 1 410m, 1 380m, 1 345w, 1 270m, 1 210w, 1 080brs, 875m, and 750s cm^{-1}.

1,2,4,6-Tetraphenylpyridinium Perchlorate.—The salt (0.5 g) in MeOH (300 ml) was photolysed at 300 nm for 24 h as described above. The solid product was recrystallised from MeOH as yellow needles to give 2-*phenylbenzo*[8,9]-*quinolizino*[4,5,6,7-fed]*phenanthridinylium perchlorate* (7a) (0.42 g, 85%), m.p. 340·°C (decomp.) (Found: C, 72.2; H, 3.7; N, 2.9. C$_{29}$H$_{18}$ClNO$_4$ requires C, 72.5; H, 3.8; N, 2.9%); $v_{max.}$ (Nujol) 1 625s, 1 600m, 1 525m, 1 485m, 1 445m, 1 410m, 1 340m, 1 295m, 1 080br, 855w, 745s, and 680s cm^{-1}. Similar photocyclisation (300 nm, 24 h) of the corresponding pyridinium chloride (0.5 g) gave the corresponding *chloride* (0.46 g, 93.5%), m.p. 340 °C (decomp.) (Found: C, 81.6; H, 4.5; Cl, 8.3; N, 3.4. C$_{29}$-H$_{18}$ClN·0.5H$_2$O requires C, 82.0; H, 4.5; Cl, 8.4; N, 3.3%).

The i.r. spectrum was very similar to that of the perchlorate salt above.

Details of other benzo[*c*]pyrido[1,2-*a*][1,8]naphthyridinyl-ium and benzo[8,9]quinolizino[4,5,6,7-*fed*]phenanthridinyl-ium salts and betaines prepared by analogous photo-cyclisations are given in Table 4.

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