1,3-Dipolar Character of Six-membered Aromatic Rings. Part 45.[1] Photochemically-induced Dimerisation of 1-Vinyl- and 1-Heteroaryl-3-oxidopyridiniums and Related Compounds

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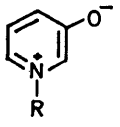
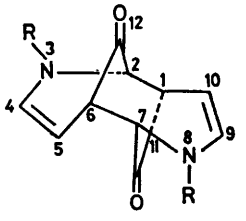
Irradiations of 1-aryl-3-oxidopyridiniums and 2-methyl-4-oxidoisoquinolinium yield photochemically allowed symmetrical dimers, further chemical transformations of which are described. 1-H, 1-methyl, and 1-benzyl-3-oxidopyridiniums are photostable. 3-Oxido-1-styrylpyridinium yields cycloadducts with a variety of 2π- and 4π-electron dipolarophiles as well as a photodimer.

3-OXIDO-1-PHENYLPYRIDINIUM [2] (6) readily [3] undergoes photochemically induced dimerisation to photodimer (15). We now describe further photochemical dimerisations of this type. 3-Hydroxy-1-styrylpyridinium chloride (19) was prepared by adaptation of the method given by Kröhnke *et al.*[4] for 1-styrylpyridinium bromide. The reaction of styrene oxide with 3-hydroxypyridine under acidic conditions yielded the pyridinium salt (21)

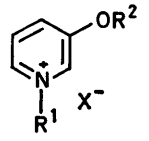


(1) R = H
(2) R = 2-Pyridyl
(3) R = 4-Pyridyl
(4) R = Styryl
(5) R = 4,6-Dimethylpyrimidin-2-yl
(6) R = Ph
(7) R = Me
(8) R = CH_2Ph
(9) R = 5-Nitro-2-pyridyl
(10) R = —CH=CH—COAr



(11) R = 2-Pyridyl
(12) R = 4-Pyridyl
(13) R = Styryl
(14) R = 4,6-Dimethylpyrimidin-2-yl
(15) R = Ph

which was dehydrated in the presence of benzoyl chloride [*via* (22)] producing the desired 3-hydroxy-1-styrylpyridinium chloride (19). The betaine, 3-oxido-1-styrylpyridinium (4), was released from the hydrochloride (19) by triethylamine in acetonitrile. Irradiation of the styryl betaine (4) ($\lambda_{max.}$ 351 nm) in EtOH–EtOAc yielded the yellow crystalline photodimer (13), m.p. 192—194 °C.



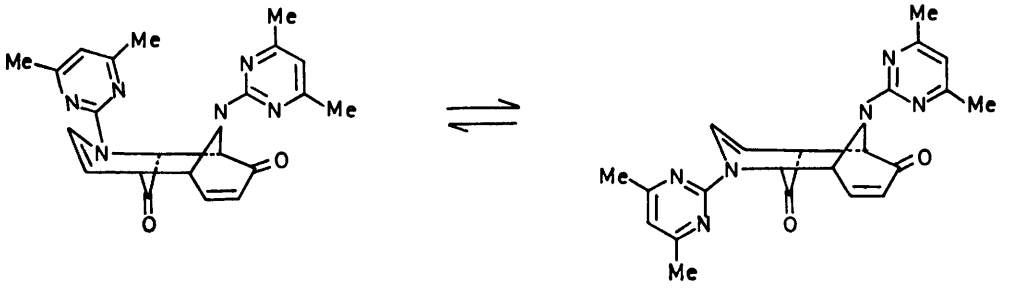
(16) R^1 = 4,6-Dimethylpyrimidin-2-yl, X = Cl, R^2 = H
(17) R^1 = 2-Pyridyl, X = Cl, R^2 = H
(18) R^1 = 4-Pyridyl, X = Cl, R^2 = H
(19) R^1 = Styryl, X = Cl, R^2 = H
(20) R^1 = Styryl, X = ClO_4, R^2 = H
(21) R^1 = $PhCH(OH)CH_2$, X = Cl, R^2 = H
(22) R^1 = Styryl, X = Cl, R^2 = COPh
(23) R^1 = Styryl, X = Br, R^2 = H
(24) R^1 = $PhCH(OH)CH_2$, X = Br, R^2 = H
(25) R^1 = Styryl, X = Br, R^2 = COPh

Irradiation of 3-oxido-1-(2-pyridyl)pyridinium (2) [5] [in EtOH–EtOAc (1 : 1)] and 3-oxido-1-(4-pyridyl)-pyridinium (3) [5] in water ($\lambda_{max.}$ 336 and 334 nm, respectively) also yielded the crystalline photodimers (11), m.p. >200 °C (decomp.) and (12), m.p. >220 °C (decomp.), respectively. Similarly, photoirradiation of 3-oxido-1-(4,6-dimethylpyrimidin-2-yl)pyridinium (5) [derived from the thermal dimer (26) [6]] produced the photodimer (14), m.p. 256—257 °C.

3-Hydroxypyridine (which exists partly as the pyridinium tautomer [7]) (1), 1-methyl-3-oxidopyridinium [8] (7), 1-benzyl-3-oxidopyridinium [9] (8), and 3-oxido-1-(5-nitro-2-pyridyl)pyridinium [6] (9) ($\lambda_{max.}$ 315, 320, 324, and 354 nm, respectively, were irradiated in water but all betaines were photostable. 1-Methyl- and 1-benzyl-3-oxidopyridinium are also photostable in the presence of benzophenone [10] as photosensitiser. The observed photo-unreactivity of these betaines is in agreement with their known [8,9] unreactivity towards thermal dimerisation. Other betaines containing photosensitive substituents [*e.g.* betaines (10) [11]] decomposed to complex mixtures on photoirradiation (at 346 nm).

A variety of attempted photocycloadditions, *e.g.*, of anthracene and diphenylacetylene, to 3-oxido-1-phenylpyridinium (6) were unsuccessful.

Structural Assignment of Dimers.—The mass spectra of each of three dimers (11)—(13) exhibited the appropriate

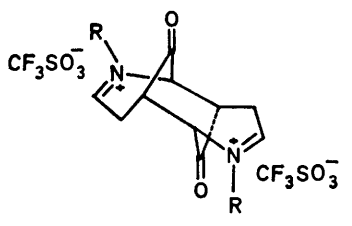


(26)

parent molecular ion ($M^{+\cdot}$) together with the corresponding betaine ion ($M^{+\cdot}/2$) [*e.g.* dimer (13) $M^{+\cdot}$ 394, $M^{+\cdot}/2$ 197], while dimer (14) shows only the betaine ion ($M^{+\cdot}/2$). The elemental analysis of each of the four compounds was consistent with the dimeric formulation: *e.g.*, dimer (12), $C_{20}H_{16}N_4O_2$. The i.r. spectra of each of the dimers exhibited a ν(C=O) band at 1 740—1 752 cm^{-1} characteristic of a saturated ketone: *e.g.* dimer (11) showed ν(C=O) at 1 740 cm^{-1}.

The n.m.r. spectra (Table 1) clearly established the structures (11)—(14) as (1*SR*,2*RS*,6*RS*,7*SR*)-3,8-disubstituted-3,8-diazatricyclo[5.3.1.$1^{2,6}$]dodeca-4,9-diene-11,12-diones analogous to the known 3,8-diphenyl derivative (15).[3] The pair of bridgehead protons 1- and 6-H give rise to an overlapping doublet of triplets (coupling with 2- and 7-H, and 10- and 5-H, and long-range W type coupling with 7- and 2-H). The second pair of bridgehead protons, 2- and 7-H, give a triplet (coupling with 1- and 6-H and long-range W type coupling with 6- and 1-H). The vinylic pair 5- and 10-H give a double doublet (*cis*-vicinal coupling with 4- and 9-H and vicinal coupling with the bridgehead protons 6- and 1-H). The olefinic pair 4- and 9-H give a doublet by *cis*-coupling with 5- and 10-H. The *exo*-stereochemistry is clearly defined by the small coupling constant (J 2.0—3.3 Hz) between 1- and 2-H and 6- and 7-H (the dihedral angle of *ca.* 50° corresponds [12] to a calculated J of *ca.* 3 Hz).

After standing in trifluoroacetic acid, the dimers (11)—(13) exhibit much simplified n.m.r. spectra consistent with the di-immonium structures (27).



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Irradiation of Bicyclic Betaines.—Photoirradiation in water of 1-methyl-3-oxidoquinolinium [13] ($\lambda_{max.}$ 382 nm) yielded a yellow photodimer, m.p. 175 °C. The dimeric structure was established by mass spectrometry ($M^{+\cdot}$ 318) and elemental analysis ($C_{20}H_{18}N_2O_2$). The i.r. spectrum which shows a single ν(C=O) at 1 740 cm^{-1} suggests a symmetrical dimeric structure (28) or (29). The n.m.r. spectrum in $CDCl_3$ also supports these structures since there is only one signal for the protons

TABLE 1

^{1}H N.m.r. spectra of photodimers [a, b]

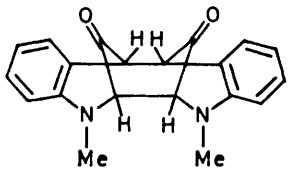
	(11) [c]	(12) [c]	(13) [d]	(14) [c]	(15)
Chemical shifts (δ)					
1	3.81 [f]	3.81 [f]	3.24 [f]	3.84 [f]	3.19 [f]
2	5.03 [g]	5.13 [g]	4.31 [g]	5.53 [g]	4.35 [g]
4	7.10 [h]	7.26 [h]	4.69 [h]	7.43 [h]	6.59 [h]
5	5.60 [i]	5.72 [i]	6.68 [i]	5.66 [i]	4.63 [i]
6	3.81 [f]	3.81 [f]	3.24 [f]	3.84 [f]	3.19 [f]
7	5.03 [g]	5.13 [g]	4.31 [g]	5.53 [g]	4.35 [g]
9	7.10 [h]	7.26 [h]	4.69 [h]	7.43 [h]	6.59 [h]
10	5.60 [i]	5.72 [i]	6.68 [i]	5.66 [i]	4.63 [i]
CH_3				2.71	
NC*H*=CHPh			7.04 [h]		
NCH=C*H*Ph			5.72 [h]		
Aromatic	7.2—8.0 [j]	7.46—8.45 [j]	6.9—7.3 [j]	7.12 [k]	6.7—7.3 [j]
Coupling constants (J/Hz)					
1,2	2.0	2.0	3.0	3.3	3.3
1,7	2.5	2.0	3.0	3.0	1.5
1,10	6.0	6.0	6.0	6.0	6.0
2,6	2.5	2.0	3.0	3.0	1.0
4,5	8.0	8.0	8.0	8.0	7.6
5,6	6.0	6.0	6.0	6.0	6.0
6,7	2.0	2.0	3.0	3.3	3.3
9,10	8.0	8.0	8.0	8.0	7.6

[a] In p.p.m. relative to internal Me_4Si. [b] Determined at 100 MHz. [c] In CF_3CO_2H. [d] In $(CD_3)_2SO$. [e] In $CDCl_3$. [f] Double triplet. [g] Triplet. [h] Doublet. [i] Double doublet. [j] Multiplet. [k] Singlet.

of the two *N*-methyl groups at δ 3.00. The large coupling constant (J 10 Hz) for the bridgehead protons suggests that the cyclohexanedione moiety exists in the boat conformation. The n.m.r. spectrum in $(CD_3)_2SO$ exhibits two *N*-methyl signals; the reason for this is not clear.

The isomeric 2-methyl-4-oxidoisoquinolinium [(32; R = Me)] [14] ($\lambda_{max.}$ 367 nm) on irradiation in EtOAc yielded the photoisomer (31). Compound (31) was shown to be an isomer of (32; R = Me) by mass spectrometry (*m/e* 159). The i.r. spectrum shows a ν(C=O) at

1 718 cm^{-1} characteristic of an αβ-unsaturated ketone in a five-membered ring. The n.m.r. spectrum clearly demonstrates structure (31): the bridgehead protons, 1- and 3-H give doublets by *cis*-coupling ($J_{1,3}$ 4.0 Hz).



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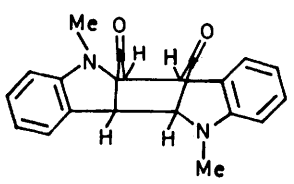

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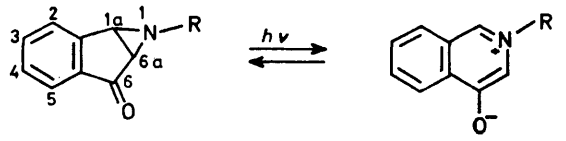
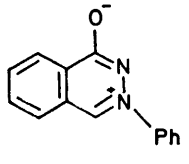


(30)
(31) R = Me

(32)

The *N*-methyl group exhibits a three-proton singlet at δ 2.27. In the isoquinolinium series, Hansen and Undheim reported [15] the reversible photochemically allowed valence isomerism between 1-aryl-1*a*,6*a*-dihydroindeno[1,2-*b*]azirin-6(1*H*)-ones (30; R = aryl) and 2-aryl-4-oxidoisoquinolinium (32; R = aryl).

Irradiation of 1-oxido-3-phenylphthalazinium [16] (33) ($\lambda_{max.}$ 350 nm) in water yielded a green solid, m.p. 136—138 °C. A dimeric structure was indicated by the mass spectrum ($M^{+\cdot}/2$). The i.r. spectrum exhibited a single ν(C=O) at 1 690 cm^{-1}. The available evidence at this time suggests that the dimeric structure is (34) but insolubility prevented a decisive n.m.r. spectrum from being obtained. The isomeric 2-substituted 4-oxidocinnoliniums have been reported [17] to undergo photochemically induced molecular rearrangement.



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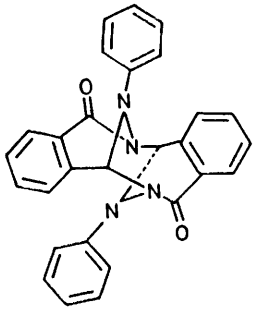

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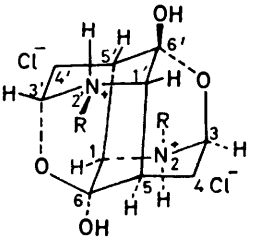
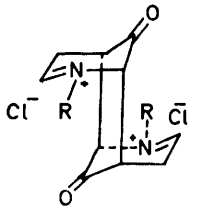
Transformation of Photodimer.—The photodimer (13) was readily converted to the bis-hemiacetal salt (35), m.p. 230 °C, with hot dilute HCl. The formation of this salt probably involves the intermediacy of the immonium salt (37). Attempts to convert the bis-hemiacetal salt (35) to the free base proved unsuccessful. Presumably the α-aminoalcohol of the free base is subject to further hydrolysis.

The ^1H n.m.r. spectrum of the bis-hemiacetal confirmed structure (35). The 1-H proton gives a triplet at δ 4.07 through geminal coupling with 5′-H and W type long-range coupling with 5-H. The complex pattern for 3-H at δ 5.50 is the result of two vicinal couplings with 4α- and 4β-H, and W type coupling to 5-H. We recently described [18] the formation of the *NN*′-diphenyl bis-hemiacetal salt (36) in a similar acid-catalysed cyclisation of the photodimer (15) of 3-oxido-1-phenylpyridinium (6).

Thermal Cycloadditions.—3-Oxido-1-styrylpyridinium (4) readily undergoes thermal cycloadditions at the 2- and 6-positions with 2π-electron addends, and at the 2- and 4-positions with 4π-electron addends. Ethyl acrylate and acrylonitrile yielded the *exo*-adducts (40) and (41) of expected regio- and stereo-chemistry. Likewise, 2-chloroacrylonitrile yielded a single regioisomer (38), m.p. 124 °C. In the reaction with styrene, the *N*-styryl



(35) R = H
(36) R = Ph



(37) R = CH=CHPh

betaine yielded the expected *endo*-cycloadduct (42) as the sole product. *N*-Phenylmaleimide produced a single unstable cycloadduct (43), presumably of *exo*-stereochemistry, which rapidly decomposed in solution (*cf.* 1-aroyloxy-3-oxidopyridinium reacts with *N*-phenylmaleimide to realise a single *exo*-cycloadduct [11]). Diethyl fumarate readily reacted with the betaine to yield the 6-*exo*,7-*endo*-compound (39), m.p. 180—181 °C. The isomeric 6-*endo*,7-*exo*-compound was not detected in the reaction mixture (*cf.* 3-oxido-1-phenylpyridinium [19] from which both *trans*-isomers were obtained). The i.r. spectra of all 2,6-adducts exhibit a characteristic broad carbonyl band for the αβ-unsaturated ketone (see Experimental section). Further confirmation of cycloadduct structure was furnished by n.m.r. spectroscopy (see Table 2).

The 4π-electron addend, 2,3-dimethylbuta-1,3-diene with the *N*-styryl betaine yielded the 2,4-adduct (44). The i.r. spectrum exhibits a carbonyl band at 1 720 cm^{-1} for the saturated ketone, and a ν(C=C) at 1 640 cm^{-1} for the enamine double bond.

The *N*-styryl cycloadducts (38)—(44) are all unstable (*cf.* instability of *N*-styrylpiperidine [20]). Compounds (38) and (39) may be isolated as pure crystalline solids which, however, decompose on repeated recrystallisation. The *N*-phenylmaleimide adduct (43) is very

TABLE 2

^{1}H N.m.r. spectra of thermal cycloadducts [a,b]

Chemical shifts (δ)

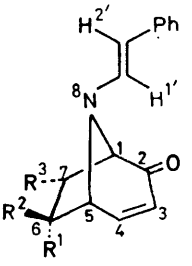
		(38) [c]	(39) [c]	(40) [c]	(41) [c]	(42)
	1	4.20 [d]	4.26 [d]	4.44 [d]	4.38 [d]	4.47 [d]
	3	6.14 [d]	5.92 [d]	5.93 [d]	5.92 [d]	6.02 [d]
	4	6.96 [d]	6.90 [d]	6.90 [d]	*e*	*e*
	5	4.74 [f]	4.59 [f]	4.56 [f]	4.57 [f]	4.70 [d]
6-*endo*			3.49 [f]	3.04 [d]	3.03 [d]	
6-*exo*						4.10 [g]
7-*endo*		2.18 [f]		2.15 [d]	2.13 [d]	2.16 [d]
7-*exo*		3.46 [d]	3.41 [d]	3.43 [g]	3.47 [g]	3.08 [g]
	1′	6.55 [f]	6.47 [f]	6.47 [f]	6.45 [f]	6.55 [f]
	2′	5.51 [f]	5.45 [f]	5.45 [f]	5.47 [f]	5.47 [f]
C_6H_5		7.13 [h]	7.08 [h]	7.14 [h]	7.17 [h]	7.26 [h]
CH_2			4.11 [i]	4.09 [i]		
CH_3			1.24 [j]	1.23 [j]		

Coupling constants (*J*/Hz)

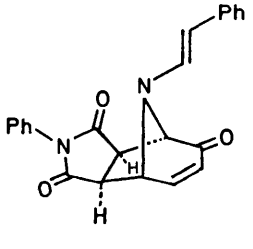
		(38)	(39)	(40)	(41)	(42)
	1,3	2.0	2.0	2.0	2.0	2.0
1,7-*exo*		8.0	7.0	7.5	8.0	8.0
	3,4	10.0	11.0	10.0	10.0	10.0
	4,5	6.0	5.5	5.5	6.0	*e*
	5,6					6.0
6-*endo*, 7-*endo*				9.5	10.0	
6-*endo*, 7-*exo*			4.0	4.0	4.0	
6-*exo*, 7-*endo*						7.0
6-*exo*, 7-*exo*						10.0
7-*endo*, 7-*exo*		15.0		14.0	14.0	14.0
	1′,2′	14.0	14.0	14.0	14.0	14.0

[a] In p.p.m. relative to internal Me_4Si. [b] Determined at 100 MHz. [c] In $CDCl_3$. [d] Double doublet. [e] Not measurable due to signal overlap. [f] Doublet. [g] Double triplet. [h] Multiplet. [i] Quartet. [j] Triplet.

unstable and decomposes in solution. All the *N*-styryl cycloadducts yield phenylacetaldehyde on decomposition.



(38) R^1 = CN or Cl, R^2 = CN or Cl, R^3 = H
(39) R^1 = H, R^2 = R^3 = CO_2Et
(40) R^1 = R^3 = H, R^2 = CO_2Et
(41) R^1 = R^3 = H, R^2 = CN
(42) R^1 = Ph, R^2 = R^3 = H



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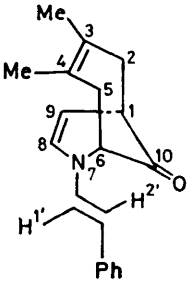

(44)

EXPERIMENTAL

M.p.s were determined with a Reichert apparatus. Spectra were recorded with a Perkin-Elmer model 257 i.r. grating spectrophotometer, a Perkin-Elmer SP 800 u.v. spectrophotometer, a Hitachi–Perkin-Elmer RMU-6E mass spectrometer, and a Varian HA-100 n.m.r. spectrometer.

Compounds were purified until they were observed as single spots on t.l.c. (Kieselgel PF 254). Solvents and reagents used in irradiation experiments were dried by the following methods: EtOH, Mg method; EtOAc, distilled from K_2CO_3; Et_3N, NaOH; MeCN, molecular sieves.

Irradiations with an internal light source were performed with a medium-pressure arc, type Hanovia PCR 1L, and water-cooled Pyrex containers were used. A Pyrex immersion well was used to absorb radiation <3 000 Å. All irradiations were performed at 25—35 °C.

Irradiations with an external light source were performed with a Rayonet reactor (RPQ-100), with 3 500 Å lamps, in quartz flasks at 60 °C.

3-*Hydroxy*-1-(2-*hydroxy*-2-*phenylethyl*)*pyridinium Chloride* (21).—A solution of 3-hydroxypyridine (4.75 g, 50 mmol), styrene oxide (6.0 g, 50 mmol), and glacial acetic acid (4 g) in EtOH (16 g) were heated under reflux for 6 h. The cooled yellow solution was treated with concentrated HCl (7 ml) to yield the *chloride* (21) (2.5 g, 20%) as microcrystals, m.p. 233—234 °C (EtOH) (Found: C, 61.7; H, 5.8; N, 5.4. $C_{13}H_{14}ClNO_2$ requires C, 62.0; H, 5.6; N, 5.6%); $\nu_{max.}$ ($CHBr_3$) 3 280, 3 000—2 500, 1 600, 1 520, 1 505, 1 455, 1 410, 1 324, 1 270, 1 265, 1 095, 1 065, and 1 030 cm^{-1}.

3-*Benzoyloxy*-1-*styrylpyridinium Chloride* (22).—3-Hydroxy-1-(2-hydroxy-2-phenylethyl)pyridinium chloride (6.00 g, 24 mmol) and benzoyl chloride (25 ml) were heated (180—190 °C) for 1 h. The cooled (0 °C) mixture was treated with Me_2CO (15 ml). After 14 h, the *title compound* (22) (4.5 g, 56%) was obtained as microcrystals, m.p. 160—165 °C (decomp.) (EtOH) (Found: C, 64.2; H, 3.7; N, 5.1. $C_{20}H_{16}ClNO_2,2H_2O$ requires C, 64.3; H, 3.8; N, 5.4%); $\nu_{max.}$ ($CHBr_3$) 3 650—3 200, 2 920, 1 750, 1 595, 1 580, 1 495, 1 490, 1 450, 1 400, 1 224, 1 173, 1 070, 1 045, and 1 010 cm^{-1}.

3-*Hydroxy*-1-*styrylpyridinium Perchlorate* (20).—A solution of 3-benzoyloxy-1-styrylpyridinium chloride dihydrate (0.95 g, 2.5 mmol) in concentrated HCl (10 ml) was heated under reflux for 1 h. After cooling (12 h), the mixture was filtered to yield 3-hydroxy-1-styrylpyridinium chloride (19) (0.70 g, 100%) which was characterised as the *perchlorate* (20) as light yellow needles, m.p. 168 °C (EtOH) (Found: C, 52.0; H, 4.2; N, 4.7. $C_{13}H_{12}ClNO_5$ requires C, 52.5; H, 4.1; N, 4.8%); $\nu_{max.}$ ($CHBr_3$) 3 450—3 250, 3 000—2 500, 1 588, 1 576, 1 515, 1 500, 1 455, 1 400, 1 365, 1 332, 1 288, 1 265, 1 230, and 1 030 cm^{-1}.

3-*Oxido*-1-*styrylpyridinium* (4).—Et_3N (0.58 g, 5.7 mmol) was added dropwise to a suspension of 3-hydroxy-1-styrylpyridinium chloride (19) (1.33 g, 5.7 mmol) in MeCN (20 ml). The brown solution was evaporated to dryness and the residue treated with water. The *title compound* (4) (1.1 g, 100%) was isolated as a light brown powder, m.p. 138—142 °C (decomp.); $\nu_{max.}$ ($CHBr_3$) 3 600—3 200, 3 000—2 750, 1 590—1 560, 1 505, 1 490—1 470, 1 445, 1 430, 1 345, 1 320—1 290, 1 265, 1 225, 1 165, 1 030, 950, 860—850, 785, and 755 cm^{-1}; *m/e* 344.127 416 (calc. for $M^{+\cdot}$, 344.127 318) and 172.063 587 (calc. for $M^{+\cdot}/2$, 172.063 659).

(1SR,2RS,6RS,7SR)-3,8-*Distyryl*-3,8-*diazatricyclo*-

[5.3.1.1^{2,6}]*dodeca*-4,9-*diene*-11,12-*dione* (13).—Anhydrous Et_3N (4 g, 38 mmol) was added to a solution of 3-hydroxy-1-styrylpyridinium chloride (1.0 g, 4.3 mmol) in a mixture of anhydrous EtOH–anhydrous EtOAc (2 : 3, 90 ml). The clear yellow solution was purged with nitrogen for 2 h and then irradiated for 3.5 h. The *title compound* (13) (0.46 g, 1.16 mmol, 54%) crystallised out as yellow needles, m.p. 192—194 °C (decomp.) (Found: N, 7.2. $C_{26}H_{22}N_2O_2$ requires N, 7.1%); $\nu_{max.}$ ($CHBr_3$) 1 752 (saturated ketone, C=O), 1 657 (C=C–N), 1 638, 1 604 (C=C), 1 460, 1 410, 1 350, 1 282, 1 220, 1 204, 1 015, and 928 cm^{-1}; *m/e* 394 ($M^{+\cdot}$) and 197 ($M^{+\cdot}/2$).

(1SR,2RS,6RS,7SR)-3,8-*Di*-(2-*pyridyl*)-3,8-*diazatricyclo*-[5.3.1.1^{2,6}]*dodeca*-4,9-*diene*-11,12-*dione* (11).—Anhydrous Et_3N (2 g, 19 mmol) was added to a suspension of 3-hydroxy-1-(2-pyridyl)pyridinium chloride [5] (1.0 g, 4.8 mmol) in EtOH–EtOAc (1 : 1, 90 ml). The resulting solution was purged with N_2 for 2 h and irradiated (internal) for 20 h. The *title compound* (11) (0.41 g, 50%) crystallised out as light green microcrystals, m.p. >200 °C (decomp.) (Found: C, 69.3; H, 4.6; N, 16.0. $C_{20}H_{16}N_4O_2$ requires C, 69.8; H, 4.7; N, 16.3%); $\nu_{max.}$ ($CHBr_3$) 1 740 (saturated ketone, C=O), 1 630 (C=C–N), 1 590, 1 580, 1 562, 1 470, 1 435, 1 400, 1 346, 1 313, 1 281, 1 240, 1 214, and 1 100 cm^{-1}; *m/e* 344 ($M^{+\cdot}$) and 172 ($M^{+\cdot}/2$).

(1SR,2RS,6RS,7SR)-3,8-*Di*-(4-*pyridyl*)-3,8-*diazatricyclo*-[5.3.1.1^{2,6}]*dodeca*-4,9-*diene*-11,12-*dione* (12).—A solution of NaOH (6 ml, 1N) was added to a solution of 3-hydroxy-1-(4-pyridyl)pyridinium chloride [5] (1.25 g, 6.0 mmol) in distilled water (90 ml). The resulting solution was purged with N_2 for 2 h and then irradiated (internal lamp) for 24 h. The *title dimer* (12) (0.12 g, 11.6%) separated as a grey powder, m.p. >220 °C (decomp.) (Found: C, 69.3; H, 4.8; N, 16.0. $C_{20}H_{16}N_4O_2$ requires C, 69.8; H, 4.7; N, 16.3%); $\nu_{max.}$ ($CHBr_3$) 1 745 (saturated ketone, C=O), 1 638 (C=C–N), 1 595, 1 560, 1 510, 1 440, 1 408, 1 352, 1 315, 1 297, 1 266, 1 243, 1 225, 995, and 955 cm^{-1}; *m/e* 344 ($M^{+\cdot}$) and 172 ($M^{+\cdot}/2$).

(1SR,2RS,6RS,7SR)-3,8-*Bis*-(4,6-*dimethylpyrimidin*-2-*yl*)-3,8-*diazatricyclo*[5.3.1.1^{2,6}]*dodeca*-4,9-*diene*-11,12-*dione* (14).—A solution of the dimer (26) (0.15 g, 0.37 mmol) in absolute EtOH (100 ml) was purged with N_2 for 1 h and then irradiated for 3 h at 60 °C. The resulting brown solid (0.07 g) crystallised from chloroform to yield the *title compound* (14) (0.035 g, 23%) as microcrystals, m.p. 256—257 °C (decomp.) (Found: C, 65.3; H, 5.6; N, 20.6. $C_{22}H_{22}N_6O_2$ requires C, 65.7; H, 5.5; N, 20.9%); $\nu_{max.}$ (Nujol) 1 748 (saturated ketone, C=O) and 1 642 cm^{-1} (enamine, C=C); *m/e* 201 ($M^{+\cdot}/2$, 100%).

Dimerisation of 1-*Methyl*-3-*oxidoquinolinium*.—Et_3N (0.7 g, 7 mmol) was added to a suspension of 3-hydroxy-1-methylquinolinium iodide [21] (1.0 g, 3.5 mmol) in water (95 ml). The mixture was purged with N_2 for 2 h and irradiated for 22 h. The *dimer* (28)–(29) (0.21 g, 0.66 mmol, 38%) separated and crystallised from ethanol as yellow microcrystals, m.p. 175 °C (decomp.) (Found: N, 8.8. $C_{20}H_{18}N_2O_2$ requires N, 8.8%); $\nu_{max.}$ ($CHBr_3$) 3 000—2 800, 1 740 (saturated ketone, C=O), 1 605, 1 580, 1 500, 1 480, 1 460, 1 440, 1 378, 1 324, 1 280, 1 263, 1 253, 1 235, 1 218, 1 075, 1 045, and 1 005 cm^{-1}; *m/e* 318 ($M^{+\cdot}$) and 159 ($M^{+\cdot}/2$); δ[$(CD_3)_2SO$] 2.61 (3 H, s, Me), 2.95 (3 H, s, Me), 3.10 (1 H, dd, *J* 10, 4 Hz, CH), 3.70 (1 H, dd, *J* 10, 4 Hz, CH), 3.88 (1 H, d, *J* 4 Hz, CH), 3.94 (1 H, d, *J* 4 Hz, CH), 5.85 (1 H, d, *J* 9 Hz, ArH), and 7.2—6.2 (m, ArH).

1-*Methyl*-1a,6a-*dihydroindeno*[1,2-b]*azirin*-6(1H)-*one* (31).—Et_3N (5 ml) was added to a solution of 4-hydroxy-2-methylisoquinolinium iodide [14] (1.4 g, 4.8 mmol) in EtOAc (85 ml). The solution was purged with N_2 and then irradiated (internal) for 10 h. The dark brown solution was evaporated to dryness and the residue was dissolved in CH_2Cl_2, washed with water, dilute NaOH solution, and water. Evaporation of the organic layer yielded the *title compound* (31) as a brown gum which was not further purified, $\nu_{max.}$ ($CHBr_3$) 1 718 (αβ-unsaturated ketone, C=O), 1 610 (aryl C=C), 1 474, 1 460, 1 355, 1 321, 1 285, 1 275, 1 215, 1 210, and 1 184 cm^{-1}; δ($CDCl_3$) 2.27 (3 H, s, Me), 2.48 (1 H, d, *J* 4 Hz, 1a-H), 3.00 (1 H, d, *J* 4 Hz, 6a-H), and 6.9—7.8 (4 H, m, ArH); *m/e* 159 ($M^{+\cdot}$).

Dimerisation of 1-*Oxido*-3-*phenylphthalazinium*.—A solution of 1-oxido-3-phenylphthalazinium (38) (0.80 g, 0.36 mol) in water (200 ml) was purged with N_2 for 2 h and then irradiated (internal) for 20 h. The yellow solution was filtered to yield the *dimer* (34) (0.30 g, 37.5%) as a green powder, m.p. 136—138 °C, which could not be purified; $\nu_{max.}$ ($CHBr_3$) 1 690 (amide, C=O), 1 600 (aryl C=C), 1 510, 1 490, 1 468, 1 390, 1 350, 1 230, and 1 205 cm^{-1}; *m/e* 329, 238, and 222 ($M^{+\cdot}/2$).

2,11-*Dihydroxy*-3,10-*dioxa*-5,13-*diazadiamantane Bishydrochloride* (35).—The dimer (13) (0.40 g, 1 mmol) and aqueous HCl (5 ml, 2N) were heated on a steam-bath for 1.5 h. The cooled solution was treated with acetone (200 ml) to yield the *bishydrochloride* (35) (0.28 g, 0.95 mmol, 95%) as a granular solid, m.p. 230 °C (decomp.) (water) (Found: C, 40.5; H, 5.4; N, 9.2. $C_{10}H_{16}Cl_2N_2O_4$ requires C, 40.2; H, 5.4; N, 9.4%); $\nu_{max.}$ ($CHBr_3$) 3 490, 3 380, 3 300—3 200, 1 530, 1 588, 1 578, 1 490, 1 450, 1 435, 1 415, 1 388, 1 376, 1 332, 1 290, 1 250, 1 220, 1 115, 1 074, 1 048, 1 020, 1 000, 978, and 968 cm^{-1}; δ(D_2O) * 4.07 (2 H, t, 1′-, 1-H), 5.50 (2 H, m, 3′-,3-H), 2.37 (4 H, m, 4′-,4-H), and 2.89 (2 H, t, 5′-,5-H).

3-*Hydroxy*-1-(2-*hydroxy*-2-*phenylethyl*)*pyridinium Bromide* (24).—3-Hydroxypyridine (38.8 g, 0.40 mol) and styrene bromohydrin [22] (81.2 g, 0.40 mol) were heated on a water-bath for 8 h. The solid product was triturated with acetone to give the *title compound* (24) (52.7 g, 44.1%) as microcrystals, m.p. 218—220 °C (EtOH) (Found: C, 52.8; H, 4.6; N, 4.7. $C_{13}H_{14}BrNO_2$ requires C, 52.7; H, 4.8; N, 4.7%); $\nu_{max.}$ (KBr) 3 200—3 500 (OH), 2 900—3 100 (C–H), 1 632, 1 590, 1 513, 1 495, 1 450, 1 312, 1 240, 1 210, 1 198, 1 158, 1 088, 1 060, 1 037, and 1 028 cm^{-1}.

3-*Benzoyloxy*-1-*styrylpyridinium Bromide* (25).—The bromide salt (24) (52.7 g, 0.18 mol) and benzoyl chloride (25.29 g, 0.18 mol) were heated at 195 °C for 1 h. The mixture was cooled and triturated with acetone. The *title compound* (25) (51.1 g, 75.2%) was isolated as a semihydrate forming hygroscopic microcrystals, m.p. 123—124 °C (EtOH) (Found: C, 61.3; H, 4.3; N, 3.6. $C_{20}H_{16}BrNO_2,0.5H_2O$ requires C, 61.4; H, 4.4; N, 3.6%); $\nu_{max.}$ (KBr) 3 200—3 500 (H_2O), 2 900—3 100 (C–H), 1 738 (C=O), 1 595, 1 580, 1 490, 1 472, 1 450, 1 239, 1 212, 1 131, 1 074, 1 058, and 1 015 cm^{-1}.

3-*Hydroxy*-1-*styrylpyridinium Bromide* (23).—The benzoyloxy salt (25) (51.1 g, 0.128 mol) in 10% HBr was heated under reflux for 90 min. The clear solution was cooled to give the *title compound* (23) (31.71 g, 85%) as light yellow microcrystals, m.p. 208—209 °C (EtOH) (Found: C, 56.0; H, 4.3; N, 4.8. $C_{13}H_{12}BrNO$ requires C, 56.1; H, 4.4; N, 5.0%); $\nu_{max.}$ (KBr) 3 300—3 500

* Numbering is non-systematic, for n.m.r. only.

(O–H), 2 700—3 100 (C–H), 1 618, 1 570, 1 495, 1 480, 1 448, 1 303, 1 238, 1 210, 1 152, and 1 021 cm^{-1}.

6-Chloro-2-oxo-8-styryl-8-azabicyclo[3.2.1]*oct-3-ene-6-carbonitrile* (38).—A suspension of 3-hydroxy-1-styrylpyridinium bromide (23) (1.1 g, 0.004 mol), 2-chloroacrylonitrile (1 ml), Et_3N (0.8 ml), and hydroquinone (40 mg) in MeCN (15 ml) were heated under reflux (75 °C) for 24 h. The mixture was evaporated to dryness and chromatographed on silica gel (EtOAc–light petroleum, 1 : 2) to yield the *title compound* (38) (0.356 g, 31.5%) as yellow prisms, m.p. 124 °C (propan-2-ol) (Found: C, 67.5; H, 4.7; N, 9.7; Cl, 12.4. $C_{16}H_{13}ClN_2O$ requires C, 67.5; H, 4.6; N, 9.8; Cl, 12.5%); $\nu_{max.}$ ($CHBr_3$) 1 704 (αβ-unsaturated ketone, C=O), 1 648 (enamine, C=C), and 1 604 cm^{-1}; $\lambda_{max.}$ (EtOH) 281 (log ε 4.27) and 221 nm (4.17); *m/e* 285 ($M^{+\cdot}$).

Diethyl 2-Oxo-8-styryl-8-azabicyclo[3.2.1]*oct-3-ene-6-exo,-7-endo-dicarboxylate* (39).—A suspension of 3-hydroxy-1-styrylpyridinium bromide (23) (1 g, 0.003 6 mol), diethyl fumarate (0.8 ml), Et_3N (0.55 ml), and hydroquinone (50 mg) in dry MeCN (15 ml) were heated under reflux (75 °C) for 5 h. The mixture was evaporated to dryness and the residue chromatographed on silica gel (EtOAc–light petroleum, 1 : 2) to yield the *title compound* (39) (0.22 mg, 16.7%) as pale yellow prisms, m.p. 180—181 °C (EtOH) (Found: N, 3.6. $C_{21}H_{23}NO_5$ requires N, 3.8%); $\nu_{max.}$ ($CHBr_3$) 1 730 (ester, C=O), 1 685 (αβ-unsaturated carbonyl, C=O), 1 640 (enamine, C=C), and 1 595 cm^{-1}; *m/e* 369 ($M^{+\cdot}$).

Ethyl 2-Oxo-8-styryl-8-azabicyclo[3.2.1]*oct-3-ene-6-exo-carboxylate* (40).—The salt (23) (0.8 g, 0.002 9 mol), ethyl acrylate (0.8 ml), hydroquinone (40 mg), and Et_3N (0.46 ml) in anhydrous MeCN (12 ml) were heated under reflux (75 °C) for 4 h. The mixture was evaporated to dryness and the residue extracted with anhydrous Et_2O. The extract was evaporated to dryness to yield a gum which was triturated with light petroleum (b.p. 80—100 °C) to remove unchanged ethyl acrylate. The *title compound* (40) was obtained as a yellow gum which could not be further purified without decomposition, $\nu_{max.}$ ($CHBr_3$) 1 730 (ester, C=O), 1 680 (αβ-unsaturated ketone, C=O), 1 640 (enamine, C=C), and 1 597 cm^{-1}.

2-Oxo-8-styryl-8-azabicyclo[3.2.1]*oct-3-ene-6-exo-carbonitrile* (41).—The salt (23) (1.0 g, 0.003 6 mol), hydroquinone (50 mg), acrylonitrile (1 ml), and Et_3N (0.55 ml) in anhydrous MeCN (15 ml) were heated at 70 °C for 6 h. The mixture was evaporated to dryness and the residue extracted with anhydrous Et_2O to yield a gum which was triturated with light petroleum (b.p. 80—100 °C) to remove unchanged acrylonitrile. The *title compound* (41) was obtained as a pale yellow gum which could not be further purified without decomposition, $\nu_{max.}$ ($CHBr_3$) 2 250 (CN), 1 685 (αβ-unsaturated ketone, C=O), 1 640 (enamine, C=C), and 1 595 cm^{-1}.

6-endo-Phenyl-8-styryl-8-azabicyclo[3.2.1]*oct-3-en-2-one* (42).—A suspension of the salt (23) (1.0 g, 0.003 6 mol), Et_3N (0.55 ml), styrene (0.8 ml), and hydroquinone (51 mg) in anhydrous MeCN (15 ml) were heated under reflux (75 °C) for 4 h. The mixture was evaporated to dryness and the residue extracted with anhydrous Et_2O. The extract was evaporated to dryness to yield a gum which was triturated with light petroleum (b.p. 80—100 °C) to remove unchanged styrene. The *title compound* (4^+) was obtained as a yellow gum which could not be further purified without decomposition, $\nu_{max.}$ ($CHBr_3$) 1 685 (αβ-unsaturated ketone, C=O), 1 640 (enamine, C=C), and 1 600 cm^{-1}.

2-Oxo-N-phenyl-8-styryl-8-azabicyclo[3.2.1]*oct-3-ene-6,7-dicarboxylic Imide* (43).—3-Hydroxy-1-styrylpyridinium bromide (23) (1.0 g, 0.003 6 mol), *N*-phenylmaleimide (0.5 g, 0.002 9 mol), Et_3N (0.55 ml), and hydroquinone (50 mg) in anhydrous MeCN were heated at 70 °C for 5 h. The mixture was evaporated to dryness *in vacuo* and the residue extracted with anhydrous Et_2O. The extract was evaporated *in vacuo* to yield the *title compound* (43) as a pale yellow gum which could not be further purified without decomposition, $\nu_{max.}$ ($CHBr_3$) 1 710 (imide, C=O), 1 685 (αβ-unsaturated ketone, C=O), 1 640 (enamine, C=C), and 1 600 cm^{-1}.

3,4-Dimethyl-7-styryl-endo-7-azabicyclo[4.3.1]*deca-3,8-dien-10-one* (44).—A mixture of 3-hydroxy-1-styrylpyridinium bromide (23) (1.018 g, 0.003 7 mol), 2,3-dimethyl-1,3-butadiene (1 ml), hydroquinone, and Et_3N (0.55 ml) in anhydrous MeCN (15 ml) were heated at 65 °C for 6 h. The reaction mixture was evaporated to dryness *in vacuo* and the residue extracted with anhydrous Et_2O. The extract was evaporated *in vacuo* to yield a gum which was triturated with light petroleum (b.p. 80—100 °C) to remove unchanged diene. The *title compound* (44) was obtained as a pale yellow gum which could not be further purified, $\nu_{max.}$ ($CHBr_3$) 1 720 (saturated ketone, C=O), 1 640 (enamine, C=C), and 1 600 cm^{-1}; δ($CDCl_3$) 1.70 (3 H, s, Me), 2.24 (3 H, overlap, 2-*endo*-, 2-*exo*-, 5-*exo*-H), 3.01 (2 H, overlap, 1-, 5-*endo*-H), 4.19 (1 H, d, $J_{6,8}$ 2.0, $J_{5\text{-}exo,6}$ 8.0 Hz, 6-H), 4.35 (1 H, dd, $J_{8,9}$ 8.0 Hz-9-H), 5.45 (1 H, d, $J_{1'2'}$ 14.0 Hz, 2'-H), 6.16 (1 H, d, 8-H), 6.59 (1 H, d, 1'-H), and 7.11 (5 H, m, Ph).

We would like to thank UNESCO, the British Council, and NATO for Postdoctoral Fellowships to S. I. B., G. M., and E.-U. W. respectively.

[8/1070 *Received*, 8*th June*, 1978]

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