Syntheses of Condensed Polycyclic Azonia Aromatic Compounds by Photocyclization

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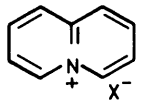
Stilbene-type photocyclization provides a good route to new condensed polycyclic azonia aromatic compounds. The structures of the new compounds so formed have been confirmed by direct comparison with independently prepared samples. The photocyclization of the 2-styrylisoquinolinium salt (**11**) and 1-[β-(2-naphthyl)vinyl]pyridinium salt (**12**) gave the dibenzo[*a*,*h*]quinolizinium salt (**14**) and the naphtho[1,2-*a*]quinolizinium salt (**16**) in 24 and 45% yields, respectively. The 2-[β-(2-naphthyl)vinyl]-isoquinolinium salt (**13**) was photocyclized to afford 2a-azoniabenzo[*ghi*]perylene perchlorate (**24**) in 30% yield. It was also found that 4-methyl-2a-azoniadibenzo[*c*,*g*]phenanthrene perchlorate (**27**), prepared from 1-(1-napthylthio)isoquinoline, upon photocyclization gave the methyl derivative of (**24**), compound (**28**). Bond formation *via* a conrotatory photocyclization is possible when the bond order (P_{rs}*) between the atoms r and s, involved in the cyclization in the excited state, has a negative value.

The azonia aromatic ring systems, where the bridgehead carbon of a condensed aromatic nucleus is replaced by a quaternary nitrogen, occur in a number of alkaloids, frequently in the reduced form, and have aroused much interest because of their physiological activity.[1] Since the synthesis of the parent quinolizinium cation (**1**) was accomplished by Boekelheide and



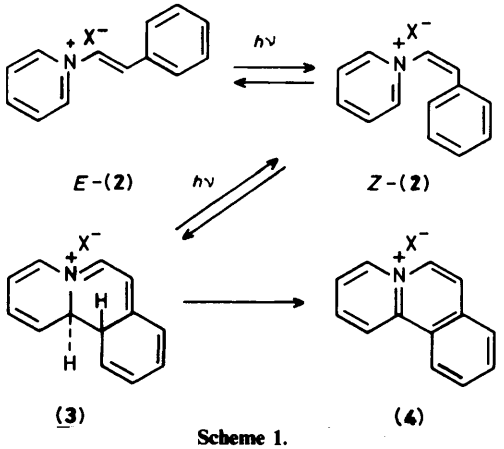
(**1**)

Gall,[2] many reports concerning the synthesis of azonia aromatic compounds have been published.[3] However, the photocyclization method, which is of great value for the synthesis of polynuclear aromatic systems, has been confined to the synthesis of benzo[*a*]quinolizinium salts.[4]

We now report the syntheses of new condensed polycyclic azonia aromatic compounds by photocyclization. The regioselectivity of the photocyclization will be also discussed.

Results and Discussion

An aerated ethanol solution of 1-styrylpyridinium salt (**2**) was irradiated with a Pyrex-filtered light (λ > 280 nm) to afford the benzo[*a*]quinolizinium salt (**4**) (60%) Figure 1 shows the time



(**3**) (**4**)

Scheme 1.

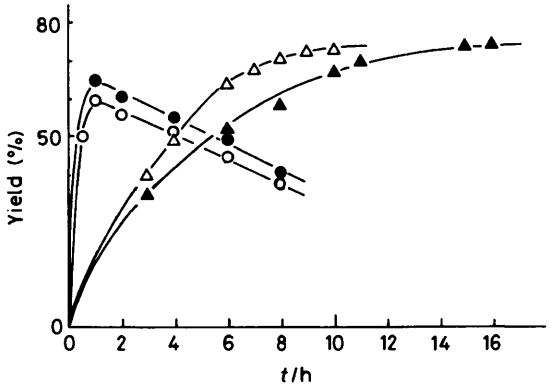


Figure 1. Photocyclization of compound (**2**) in ethanol in the air: ●: [(**8**)] = 2.5 × 10^{-4} mol dm^{-3}, in the presence of I_2; ○: [(**8**)] = 2.5 × 10^{-4} mol dm^{-3}; ▲: [(**8**)] = 5.0 × 10^{-3} mol dm^{-3}, in the presence of I_2; △: [(**8**)] = 5.0 × 10^{-3} mol dm^{-3}

course of the photocyclization of (**2**) for a 2.5 × 10^{-4} mol dm^{-3} solution, the yield being at a maximum after 1 h and then decreasing. When a 5 × 10^{-3} mol dm^{-3} solution of (**2**) was irradiated, however, the yield gradually increased and remained unchanged at maximum yield. Typically, stilbene photocyclizations are carried out in dilute solutions to minimize the competing dimerization.[5] However, this result showed that the photocyclization of (**2**) in a dilute solution (2.5 × 10^{-4} mol dm^{-3}) led to decomposition of the product (**4**). Figure 1 also indicates that the maximum yield using two oxidants, iodine and dissolved oxygen, was better than that using oxygen alone.

The photocyclization of stilbene proceeds *via* a 4a,4b-*trans*-dihydrophenanthrene which is readily dehydrogenated by air or iodine to give phenanthrene.[5,6] It was assumed that the photocyclization of (**2**) should proceed *via* a similar mechanism (Scheme 1).† Quantum chemical considerations suggest that

† Recently, an electron transfer mechanism has been proposed for the photocyclization of nitrogen hetrocyclic systems: U. C. Yoon, S. L. Quillen, P. S. Mariano, R. Swanson, J. L. Stavinoha, and E. Bay, *J. Am. Chem. Soc.*, 1983, **105**, 1204; P. S. Mariano, *Acc. Chem. Res.*, 1983, **16**, 130; Y. Kubo, N. Asai, and T. Araki, *J. Org. Chem.*, 1985, **50**, 5484.

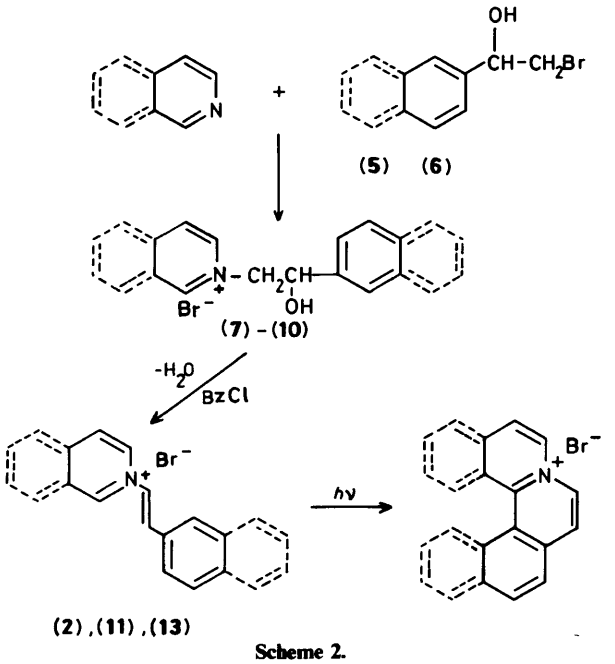
the photocyclization should occur when the energy difference between (2) and (3) is negative:

$$\Delta E = 2\,P_{rs} \cdot \beta_{rs} < 0$$

where P_{rs} and β_{rs} are the bond order and the resonance integral between the atoms r and s involved in the cyclization, respectively. Since the allowed photocyclization from *Z*-(2) to a *trans*-dihydro intermediate (3) should be conrotatory, the value of β_{rs} has a positive value. Therefore, bond formation *via* a conrotatory reaction requires a negative value of P_{rs}.[7]

In the case of (2) P_{rs} for the ground state and P_{rs}* for the excited state were calculated by Hückel MO method to be 0.076 and −0.058, respectively. This result is in accordance with the result that (2) is photocyclized to give (4).

In order to synthesize new condensed polycyclic azonia aromatic compounds, we studied the effect of the annelation of additional aromatic units to the basic 1-styrylpyridinium salt (Scheme 2). The quaternary salts (7)—(10) were obtained by the reaction of pyridine or isoquinoline with 2-bromo-1-phenylethanol (5) or 2-bromo-1-(2-naphthyl)ethanol (6). The stilbene-like molecules (2) and (11)—(13) were prepared in good yields by dehydration of the secondary alcohols (7)—(10) with benzoyl chloride. The photocyclization of the stilbene-like molecules (11)—(13) was carried out as described below.



Scheme 2.

Photocyclization of the 2-*Styrylisoquinolinium Salt* (**11**).—The photocyclization of 2-styrylisoquinolinium bromide (**11**) could, hypothetically, give the dibenzo[*a*,*h*]quinolizinium salt (**14**) and the dibenzo[*a*,*g*]quinolizinium salt (**15**). However the P_{rs}* value predicted that out of the two possible cyclization products only (**14**) should be formed (Scheme 3).

On irradiation of a solution of (**11**) (5×10^{-3} mol dm^{-3}) under conditions similar to the photocyclization of (**2**) a paper chromatogram(butan-1-ol–pyridine–water, 3:1:1) of the reaction mixture showed one spot after 3 h of irradiation. Bradsher has reported the synthesis of (**14**) by cyclodehydration of the quaternary salt derived from 1-phenylisoquinoline, and (**15**) by cyclodehydration of the quaternary salt derived from 1-formylisoquinoline and benzyl bromide.[8,9] The u.v. spectrum of the isolated product was identical with that of (**14**) prepared by independent synthesis, and was completely different from (**15**) (Table 1). I.r. and ^{1}H n.m.r. spectra were also the same as those of authentic (**14**). These results conclusively show that (**14**) is the only product in the photocyclization of (**11**).

Table 1. U.v. absorption spectra of condensed polycyclic azonia aromatic compounds

Compd.	Solvent	$\lambda_{max.}$(log ε)
(**4**)	EtOH	354 (4.10), 338 (3.96), 323 (3.67), 278 (4.28), 269 (4.23), 254 (sh), 238 (4.32), 223 (4.38)
(**14**)	EtOH	389 (4.22), 370 (4.13), 354 (3.94), 282 (4.60), 240 (4.36)
(**15**)[a]	EtOH	507, 475, 403, 383, 364, 346, 309, 296, 270, 260
(**16**)	MeOH	387 (4.04), 367 (3.97), 348 (3.94), 310 (4.37), 259 (4.43), 243 (4.38), 236 (sh), 225 (4.38)
(**18**)	EtOH	388 (4.09), 369 (4.02), 351 (4.00), 308 (4.42), 259 (4.45), 227 (4.41)
(**19**)[b]	EtOH	420 (sh), 388 (3.77), 372 (3.77), 308 (4.84), 397 (sh), 260 (4.36), 240 (4.42)
(**24**)	MeOH	435 (4.26), 412 (4.06), 394 (4.00), 376 (sh), 333 (sh), 314 (4.46), 301 (4.35), 283 (4.29), 273 (4.29), 253 (4.27), 238 (4.46), 233 (4.45), 223 (4.51)
(**27**)	EtOH	417 (4.07), 395 (3.96), 372 (3.91), 311 (4.29), 235 (4.64)

[a] Ref. 9. [b] Ref. 10.

Table 2. Photocyclization of 2-styrylisoquinolinium bromide (**11**) in air-saturated solution[a]

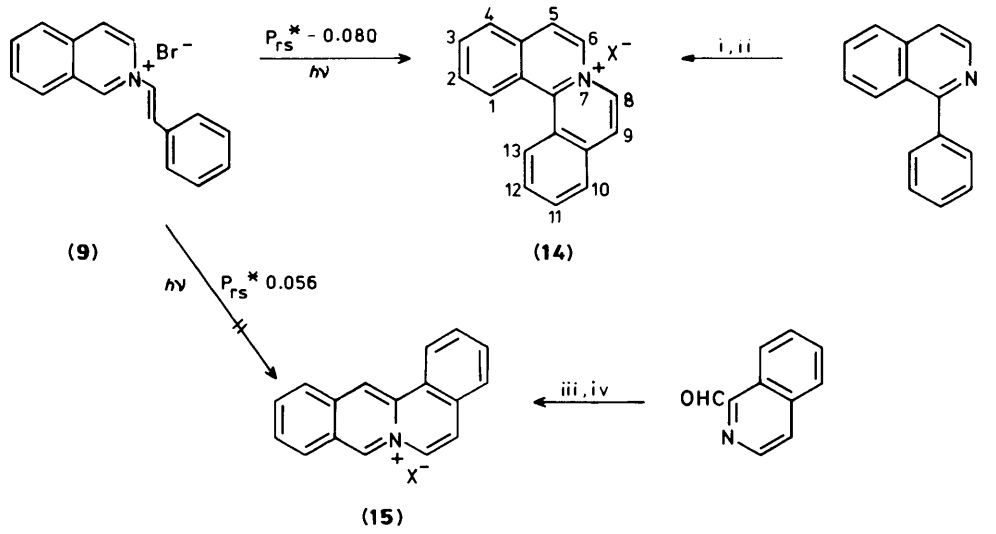
Solvent	Oxidant	Time (h)[b]	Yield (%)[c]
MeOH	O_2	3.3	44
MeOH	$O_2 + I_2$	5.0	36
EtOH	O_2	1.0	36
EtOH	$O_2 + I_2$	2.0	45
MeCN	O_2		0
MeCN	$O_2 + I_2$		0

[a] (**11**) = 5.0×10^{-3} mol dm^{-3}, $[I_2]/(11) = 0.06$, $\lambda > 280$ nm. [b] At maximum yield. [c] Determined by spectrophotometry.

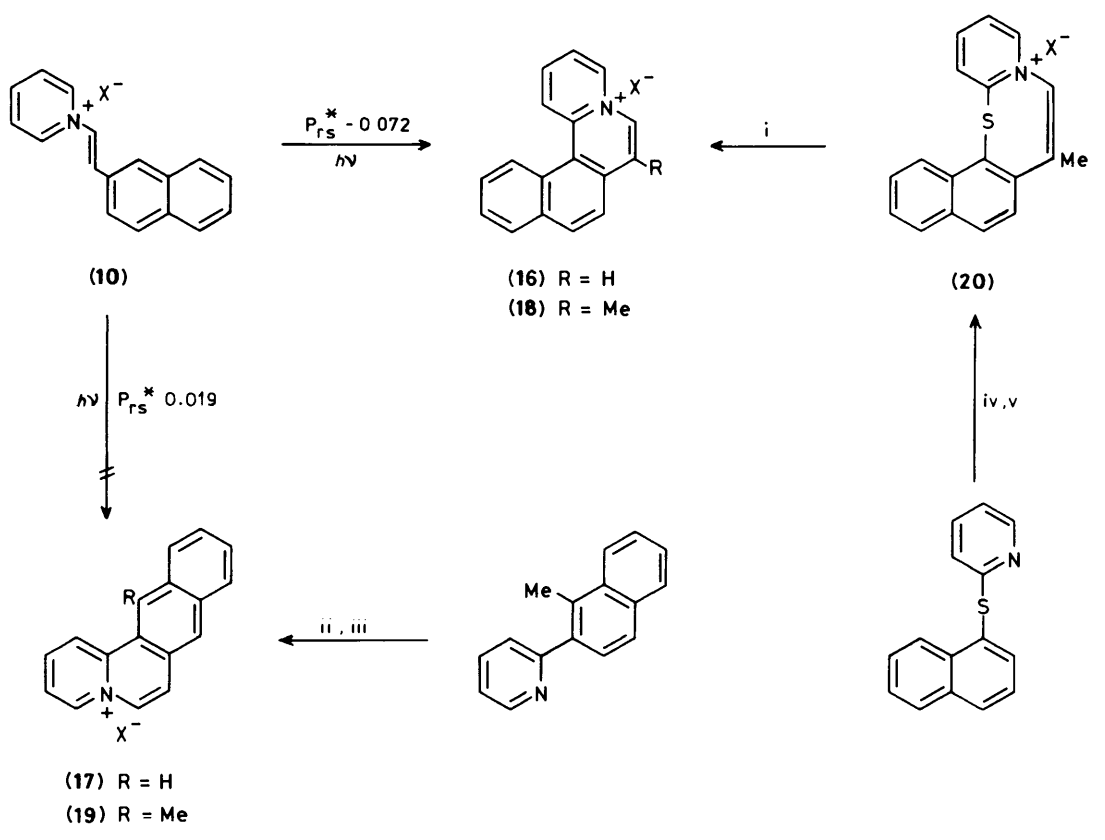
Table 2 shows the results of photocyclization of (**11**) under various conditions. In ethanol the yield of (**14**) was increased by the addition of iodine, while in methanol the presence of iodine decreased the yield. From the data in Table 2 and Figure 1 it is apparent that the irradiation time required for maximum yield using oxygen alone is shorter than that using two oxidants. It was also found that (**11**) was decomposed by irradiation in acetonitrile with or without iodine, and that (**14**) was not formed. From these results it is advantageous to carry out preparative-scale photocyclization in an air-saturated methanol solution.

Photocyclization of the 1-[β-(2-*Naphthyl*)*vinyl*]*pyridinium Salt* (**12**).—A methanol solution of 1-[β-(2-naphthyl)vinyl]-pyridinium salt (**12**) in the absence of iodine was irradiated with a Pyrex-filtered light ($\lambda > 280$ nm). The values of P_{rs}* predicted that out of the two possible cyclization products (**16**) and (**17**) only the naphtho[1,2-*a*]quinolizinium salt (**16**) should be formed (Scheme 4).

Although the unsubstituted compound (**16**) has not been reported, the methyl derivatives of (**16**) and (**17**) have been prepared, the former by sulphur extrusion from the thiazepinium salt (**20**), and the latter by cyclodehydration of 1-methyl-2-pyridylnaphthalene (see Scheme 4).[10,11] Table 1 shows that the u.v. spectrum of the isolated photoproduct is similar to that of (**18**). From this result it was concluded that the photo-



Scheme 3. *Reagents:* i, $BrCH_2CH{=}NOH$; ii, 48% HBr; iii, $PhCH_2Br$; iv, HCl



Scheme 4. *Reagents and conditions:* i, H_2O_2–AcOH, 56 °C; ii, $ClCH_2CH{=}NOH$; iii, conc. HCl; iv, $AcCH_2I$; v, PPA

cyclization product of (**12**) was (**16**), as predicted from the P_{rs}^* value.

The photocyclizations of compounds (**11**) and (**12**) gave exclusively the products resulting from cyclization at the 1-position of the naphthalene ring rather than from cyclization at the 3-position.

Photocyclization of 2-[β-(2-*Naphthyl*)*vinyl*]*isoquinolinium Salt* (**13**).—In the photocyclization of compound (**13**), out of the three possible cyclization products (**21**), (**22**), and (**23**), (**21**) is the only product predicted (Scheme 5). The field-desorption mass spectrum of the product isolated as the perchlorate salt showed a molecular ion at *m/z* 278: this pointed to the loss of perchlorate ion. Since the observed result fails to correspond to any one of the three possible cyclization products (molecular ion *m/z* 280), it seemed likely that the compound was 2a-azoniabenzo[*ghi*]perylene perchlorate (**24**), formed by further photocyclization of compound (**21**).

In order to confirm the structure, the synthesis of the methyl derivative of (**21**), compound (**27**), was performed as shown in Scheme 5. 1-(1-Naphthyl)thioisoquinoline, obtained from naphthalene-1-thiol and 1-chloroisoquinoline in 82% yield, was

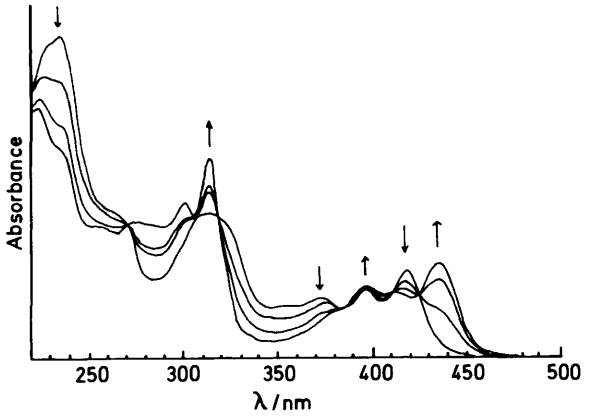
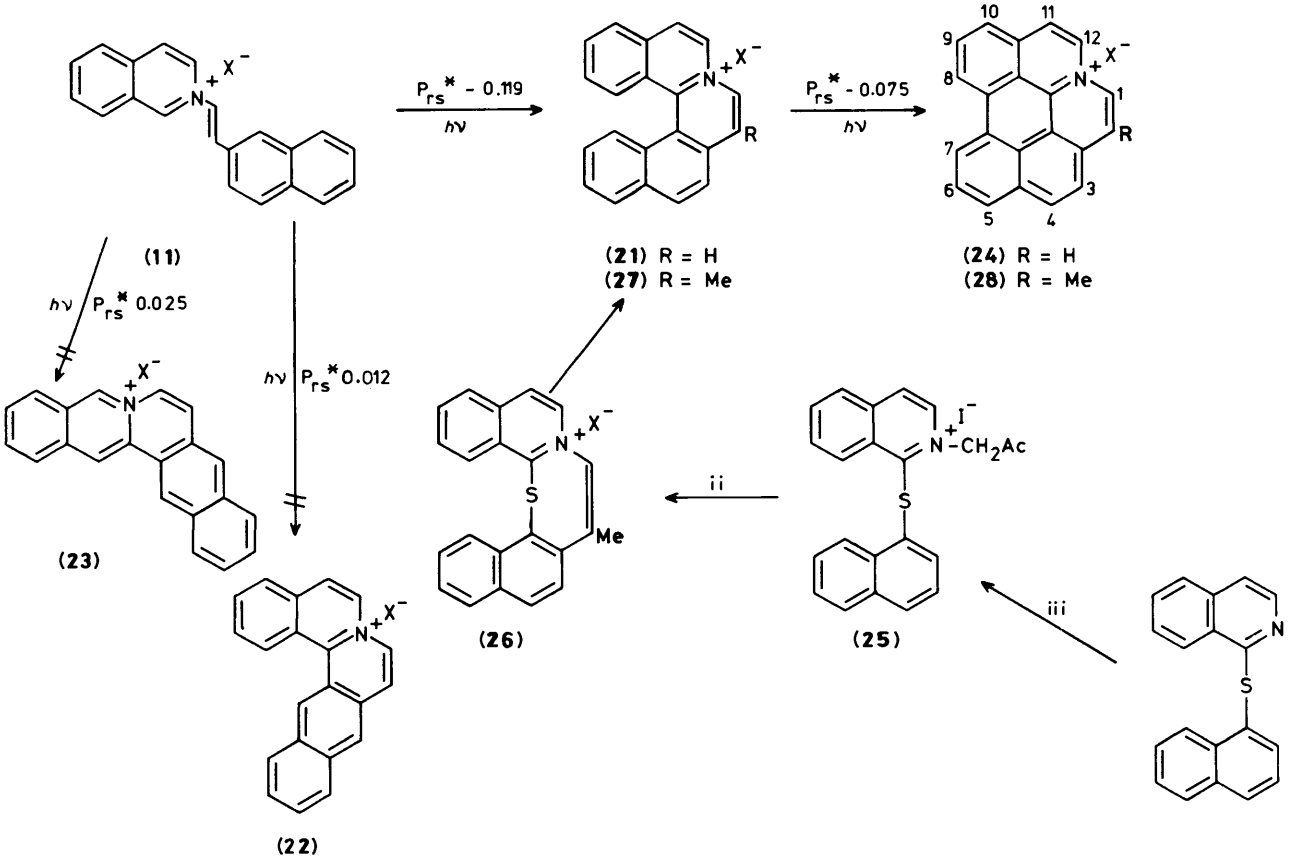


Figure 2. Photocyclization of compound (**27**) in ethanol in the air, $\lambda > 320$ nm

points were observed at 423 and 410 nm. These spectral changes showed that (**27**) was photocyclized to give (**28**). The spectrum of the photoproduct was similar to that of the photoproduct from (**13**). These results suggest that (**13**) was photocyclized to give (**21**) and then underwent further photodehydrocyclization to give (**24**).

From the P_{rs}* value (0.104), the photocyclization of (**21**) to (**24**) was, however, forbidden. This would be because the calculation of P_{rs}* was done by neglecting deviations from planarity, although (**21**) is the azonia analogue of the simplest member in the helicene series, pentahelicene. Consequently, the P_{rs}* value was calculated by considering the antibonding interaction (-0.3β) between C-10 and C-11. The P_{rs}* value (-0.075) shows that photocyclization of (**21**) may occur to give (**24**).

Our result is similar to that reported by Scholz and his co-workers,[12] who demonstrated that photocyclization of 1,2-di(2-naphthyl)ethylene (**29**) with oxygen as the only oxidant

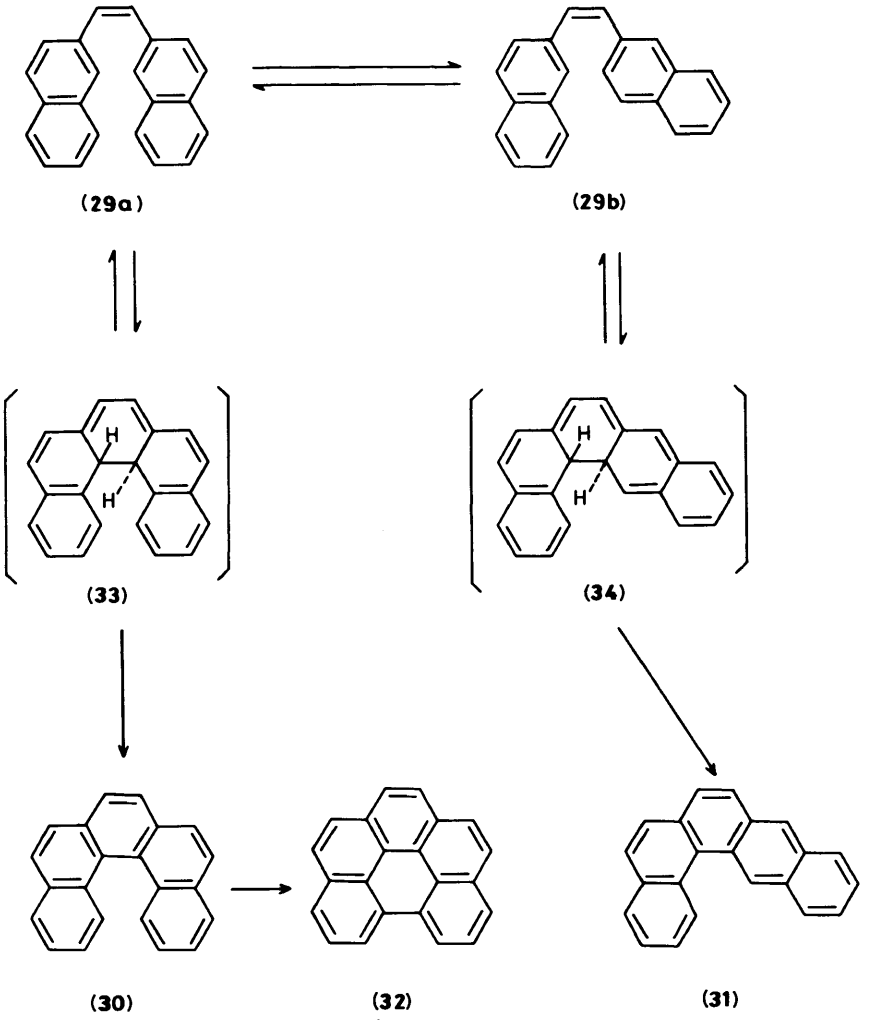


Scheme 5. *Reagents:* i, H_2O_2–CF_3CO_2H at 80 °C; ii, PPA at 150 °C; iii, $AcCH_2I$

treated with iodoacetone to give the 2-acetonyl salt (**25**) (75%). This salt was cyclized with phosphoric acid at 150 °C to give the thiazepinium salt (**26**) which underwent oxidative sulphur extrusion in the presence of hydrogen peroxide and trifluoroacetic acid at 80 °C to afford 4-methyl-2a-azoniadibenzo[*c,g*]-phenanthrene perchlorate (**27**) in 33% yield from (**25**). It is noteworthy that the oxidative sulphur extrusion in the presence of hydrogen peroxide in acetic acid, which was used for the synthesis of (**18**),[9] gave a complex mixture. The u.v. spectrum (Table 1) of the isolated product (**24**) is different from that of (**27**). An aerated ethanol solution of (**27**) was irradiated with a Pyrex-filtered high-pressure mercury lamp. Figure 2 shows that the absorbance at 417 and 372 nm decreased during irradiation, whilst new peaks appeared at 314 and 435 nm, and isosbestic afforded only benzo[*ghi*]perylene (**32**). On the other hand, Mallory reported that irradiation of an aerated solution of (**29**) in the presence of iodine gave 38% of dibenzo[*b,c*]phenanthrene (**31**), along with 25% of dibenzo[*c,g*]phenanthrene (**30**) and 37% of (**32**) (Scheme 6).[5] These results show that the yield of the oxidatively trapped product (**31**) depends on the nature and the concentration of the oxidant. Mallory describes that the ring opening of the higher-energy intermediate (**34**) to (**29b**) is much faster than that of the lower-energy intermediate (**33**) to (**29a**).[5]

Experimental

U.v. spectra were obtained with either a Shimazu UV200 or a Hitachi 220A spectrophotometer. ^{1}H N.m.r. spectra were



Scheme 6.

measured with a Hitachi R-24 spectrometer as solutions in either $(CD_3)_2SO$, $CDCl_3$, or CCl_4, using tetramethylsilane as internal standard or as solutions in trifluoroacetic acid, using sodium 3-trimethylsilylpropane-1-sulphonate as internal standard. Chemical shifts were measured in p.p.m. downfield from the internal standard. I.r. spectra were recorded with a JASCO IRA-1 spectrometer. Mass spectra were obtained with a JEOL JMS-DX 300 using electron impact or field desorption. The elemental analyses were performed on a Yanaco MT-2 CHN recorder. M.p.s measured on a Mitamura melting point apparatus, are uncorrected, whereas m.p.s determined by the capillary method are corrected.

2-Bromo-1-phenylethanol (**5**).—A mixture of bromine (15.4 g, 0.097 mol) and KBr (22.8 g, 192 mmol) in water (500 ml) was added dropwise to a vigorously stirred solution of styrene (10.1 g, 97 mmol) in water (250 ml) at 80 °C during 2 h. After cooling to room temperature, the reaction mixture was treated with 5% aqueous sodium sulphite and extracted with diethyl ether (3 × 250 ml). The combined extracts were dried ($CaCl_2$) concentrated, and distilled under reduced pressure to give the alcohol (**5**) (15.2 g, 78%), b.p. 104—105 °C (4 mmHg) (lit.,[13] 110—117 °C/2—3 mmHg); $\nu_{max.}$(neat) 3 400, 1 490, 1 445, 1 210, 1 190, 1 060, 760, and 690 cm^{-1}; $\delta(CCl_4)$ 3.17 (1 H, s, OH), 3.29 (1 H, d, *J* 7.7 Hz, CH_AH_BBr), 3.31 (1 H, d, *J* 4.9 Hz, CH_AH_BBr), 4.63 [1 H, dd, *J* 7.7 and 4.9 Hz, C*H*(OH)], and 7.10 (s, 5 H, ArH).

2-Bromo-1-(2-naphthyl)ethanol (**6**).—The reaction with 2-vinylnaphthalene (Aldrich) was carried out in a similar way to that with styrene. After being cooled to room temperature the mixture was extracted with benzene and the extract dried ($CaCl_2$) and evaporated. The residue was then chromatographed on a column of silica gel (Wakogel C300) with benzene as eluant. The second band eluted gave the alcohol (**6**) (71%) as a pale yellow oil which gradually solidified, $\nu_{max.}$(KBr) 3 400, 3 060, 1 602, 1 510, 1 222, 1 070, and 822 cm^{-1}; $\delta(CCl_4)$ 2.80 (1 H, s, OH), 3.47 (1 H, d, *J* 7.6 Hz, CH_AH_BBr), 3.50 (1 H, d, *J* 4.5 Hz, CH_AH_BBr), 5.26 [1 H, dd, *J* 7.6 and 4.5 Hz, C*H*(OH)], and 7.1—8.1 (7 H, m, ArH).

1-[2-Hydroxy-2-(2-naphthyl)ethyl]pyridinium Bromide (**9**).—A typical procedure for the preparation of the pyridinium and isoquinolinium salts (**7**)—(**10**) is described for the synthesis of compound (**9**). A mixture of 2-bromo-1-(2-naphthyl)ethanol (5.71 g, 23 mmol) and pyridine (5.20 g, 66 mmol) was heated at 100 °C for 7 h. After being cooled, the resulting orange solid was collected, washed several times with cold benzene and acetone to afford a white solid which was recrystallised from acetone–methanol to yield 1-[2-hydroxy-2-(2-naphthyl)ethyl]-pyridinium bromide as white crystals (6.04 g, 81%), m.p. 180.4—182.4 °C (corr.) (Found: C, 60.2; H, 5.05; N, 4.1. $C_{17}H_{16}NOBr \cdot \frac{1}{2}H_2O$ requires C, 60.1; H, 4.8; N, 3.95); $\nu_{max.}$(KBr) 3 240, 1 630, and 1 070 cm^{-1}; $\delta[(CD_3)_2SO]$ 5.20 (2 H, m, CH_2), 5.70 (1 H, m,

CH), 6.60 (1 H, d, *J* 5 Hz, OH), 7.8—9.5 (10 H, m, ArH), and 9.72 (2 H, d, *J* 6 Hz, pyridinium 2- and 6-H).

1-(2-*Hydroxy*-2-*phenylethyl*)*pyridinium Bromide* (**7**).—The reaction between pyridine and compound (**5**) at 90 °C for 14 h gave the title compound (**7**) (70%), m.p. 234.9—236.8 °C (white crystals from methanol) (lit.,[14] 234—235 °C) (Found: C, 55.8; H, 5.1; N, 4.7. Calc. for $C_{13}H_{14}BrNO$: C, 55.7; H, 5.0; N, 5.0%); $\nu_{max.}$(KBr) 3 240, 1 628, 1 490, 1 175, and 1 060 cm^{-1}; δ(CF_3CO_2H) 5.04 (1 H, d, *J* 6 Hz, CH_AH_B), 5.06 (1 H, d, *J* 4 Hz, CH_AH_B), 5.60 [1 H, dd, *J* 4 and 6 Hz, C*H*(OH)], and 7.4—8.8 (10 H, m, ArH).

2-(2-*Hydroxy*-2-*phenylethyl*)*isoquinolinium Bromide* (**8**).—The reaction between isoquinoline and compound (**5**) at 100 °C for 4 h gave the title compound (**8**) (64%), m.p. 167.8—169.3 °C (corr.) (white needles from pentan-1-ol) (lit.,[14] 166—168 °C) (Found: C, 58.5; H, 5.2; N, 3.9. Calc. for $C_{17}H_{16}NOBr{\cdot}H_2O$: C, 58.6; H, 5.2; N, 4.0%); $\nu_{max.}$(KBr) 3 360, 1 635, 1 160, and 815 cm^{-1}; δ(CF_3CO_2H) 5.2—5.8 [3 H, m, C*H*(OH)CH_2], 7.44 (5 H, s, PhH), 7.8—8.6 (6 H, m, isoquinolinium 3-, 4-, 5-, 6-, 7-, and 8-H), and 9.55 (1 H, s, isoquinolinium 1-H).

2-[2-*Hydroxy*-2-(2-*naphthyl*)*ethyl*]*isoquinolinium Bromide* (**10**).—The reaction between isoquinoline and compound (**6**) at 100 °C for 8 h gave the title compound (**10**) (87%), pale yellow crystals from methanol, m.p. 240.9—241.8 °C (corr.) (Found: C, 64.7; H, 4.55; N, 3.4. $C_{21}H_{18}BrNO$ requires C, 64.7; H, 4.9; N, 3.6%); $\nu_{max.}$(KBr) 3 230, 1 640, 1 080, 815, and 760 cm^{-1}; δ[$(CD_3)_2SO$] 4.6—5.7 [3 H, m, C*H*(OH)CH_2], 6.2 (1 H, br s, OH), and 7.2—9.0 (14 H, m, ArH).

1-[2-(2-*Naphthyl*)*vinyl*]*pyridinium Bromide* (**12**).—A typical procedure for the preparation of the stilbene-like compounds (**2**) and (**11**)—(**13**) is described for the synthesis of the title compound (**12**). The pyridinium bromide (**9**) (5.39 g, 18 mmol) and benzoyl chloride (12.33 g, 88 mmol) was stirred at 195 °C for 1 h. After being cooled to room temperature, the resulting solid was filtered and then washed with benzene and acetone. Recrystallisation of crude product from ethanol–methanol afforded 1-[β-(2-naphthyl)vinyl]pyridinium bromide as pale yellow needles (4.13 g, 75%), m.p. 261.6—262.8 °C (decomp., corr.) (Found: C, 65.3; H, 4.4; N, 4.1. $C_{17}H_{14}BrN$ requires C, 65.4; H, 4.5; N, 4.5%); $\nu_{max.}$(KBr) 1 650, 950, and 945 cm^{-1}; δ[$(CD_3)_2SO$] 7.5—9.0 (12 H, m, ArH and CH=CH), and 9.61 (2 H, d, 6 Hz, pyridinium 2-and 6-H); $\lambda_{max.}$(MeOH) 333 (ε 18 000 dm^3 mol^{-1} cm^{-1}), 289 (sh), 277 (13 900), and 237 nm (44 500).

1-*Styrylpyridinium Bromide* (**2**).—The pyridinium bromide (**7**) and benzoyl chloride was stirred at 200 °C for 1 h to give the title compound (**2**) (68%) (pale yellow crystals from pentan-1-ol), m.p. 161.8—162.6 °C (corr.) (lit.,[14] 154—156 °C) (Found: C, 59.1; H, 4.5; N, 5.1. Calc. for $C_{13}H_{12}BrN$: C, 59.6; H, 4.6; N, 5.3%); $\lambda_{max.}$(EtOH) 323 (log ε 4.15) and 232 nm (4.10); $\nu_{max.}$(KBr) 3 050, 1 625, 1 615, 1 605, 1 475, 950, 770, and 690 cm^{-1}; δ(CF_3CO_2H) 7.3—8.9 (10 H, m, ArH and CH=CH) and 9.16 (2 H, d, *J* 6 Hz, pyridinium 2- and 6-H).

2-*Styrylisoquinolinium Bromide* (**11**).—The isoquinolinium bromide (**8**) and benzoyl chloride was stirred at 190 °C for 1 h to give the title compound (**11**) (76%) (pale yellow needles from pentan-1-ol), m.p. 200.8—202.9 °C (corr.) (lit.,[14] 219—220 °C) (Found: C, 65.7; H, 4.4; N, 4.2. Calc. for $C_{17}H_{14}BrN$: C, 65.4; H, 4.5; N, 4.5%); $\lambda_{max.}$(MeOH) 343 (log ε 4.40), 284 (3.98), and 241 (4.40); $\nu_{max.}$(KBr) 1 635, 1 625, and 955 cm^{-1}; δ(CF_3CO_2H) 7.4—8.9 (13 H, m, ArH and CH=CH), and 9.9 (1 H, s, isoquinolinium 1-H).

2-[β-(2-*Naphthyl*)*vinyl*]*isoquinolinium Bromide* (**13**).—The isoquinolinium bromide (**10**) and benzoyl chloride was stirred at 200 °C for 1 h to give the title compound (69%) (yellowish orange crystals from methanol–ethanol), m.p. 223.7—226.2 °C (corr.) (Found: C, 68.2; H, 4.3; N, 3.55. $C_{21}H_{16}NBr{\cdot}\frac{1}{2}H_2O$ requires C, 67.9; H, 4.6; N, 3.8%); $\lambda_{max.}$(MeOH) 351 (log ε 4.32), 293 (sh), 280 (sh), 246 (4.61), and 231 nm (4.58); $\nu_{max.}$(KBr) 1 400, 1 375, 1 220, and 950 cm^{-1}; δ[$(CD_3)_2SO$] 7.2—10.6(m).

Photocyclization.—A typical photocyclization procedure is described for the synthesis of dibenzo[*a*,*h*]quinolizinium perchlorate (**14**; X = ClO_4) from compound (**11**). A solution of 2-styrylisoquinolinium bromide (780 mg, 2.5 mmol) in methanol (500 ml) in a Pyrex reaction vessel was irradiated with a 300 W high-pressure mercury lamp (Eikosha). The reaction mixture was magnetically stirred at room temperature and the progress of the photocyclization was monitored by u.v. spectroscopy. After the reaction was judged to be essentially complete, the mixture was concentrated and the residue was recrystallised from methanol–acetone to give dibenzo[*a*,*h*]quinolizinium bromide (**14**; X = Br) (184 mg, 24%), m.p. 338.8—339.9 °C (corr.) (lit.,[8] 340—342 °C) (Found: C, 65.6; H, 3.5; N, 4.2. Calc. for $C_{17}H_{12}BrN$: C, 65.8; H, 3.9; N, 4.5%). The bromide was dissolved in water and 60% aqueous perchloric acid was added to the solution. The resulting white product was filtered off, washed with cold water, and recrystallised from methanol–acetone to afford the perchlorate (**14**; X = ClO_4), m.p. 268.0—269.5 °C (corr., decomp.) (Found: C, 62.0; H, 3.6; N, 4.2. $C_{17}H_{12}ClNO_4$ requires C, 61.9; H, 3.7; N, 4.25%); $\nu_{max.}$(KBr) 3 000, 1 650, 1 490, 1 425, 1 380, 1 100, 810, and 765 cm^{-1}; δ(CF_3CO_2H) 8.0—8.5 (4 H, m), 8.93 (2 H, d, *J* 7 Hz), and 9.1—9.5 (2 H, m). Compound (**14**; X = ClO_4) was also prepared from 1-phenylisoquinoline according to a literature procedure.[8]

Benzo[a]*quinolizinium Perchlorate* (**4**; X = ClO_4).—This formed white crystals from methanol, m.p. 198.3—198.8 °C (corr.) (lit.,[15] 196—198 °C) (Found: C, 55.75; H, 3.6; N, 4.9. Calc. for $C_{13}H_{10}ClNO_4$: C, 55.8; H, 3.6; N, 5.0%); $\nu_{max.}$(KBr) 3 060, 3 040, 1 640, 1 620, 1 475, 1 100, 808, 742, and 702 cm^{-1}; δ(CF_3CO_2H) 7.8—9.5(m).

Naphtho[1,2-*a*]*quinolizinium Perchlorate* (**16**; X = ClO_4).—The pyridinium bromide (**12**) (3.22 g, 10.3 mmol) in methanol (1 l) was irradiated. After the reaction was complete, the solvent was evaporated under reduced pressure and the residue was chromatographed on a column of activated charcoal (10 g) with methanol as eluant to yield a yellow solid (2.34 g). The solid was recrystallised from methanol–ethanol to afford naphtho[1,2-*a*]-quinolizinium bromide (**16**; X = Br) as yellow needles (1.44 g, 45%). The perchlorate (**16**; X = ClO_4) was obtained by the addition of 60% aqueous perchloric acid to an aqueous solution of (**16**; X = Br). It formed pale yellow needles from methanol, m.p. 248.4—249.3 °C (corr.) (Found: C, 62.0; H, 3.5; N, 4.0. $C_{17}H_{12}ClNO_4$ requires C, 61.9; H, 3.7; N, 4.25%); $\nu_{max.}$(KBr) 3 100, 1 630, 1 600, 1 462, 1 100, 842, and 770 cm^{-1}.

2a-*Azoniabenzo*[ghi]*perylene Perchlorate* (**24**; X = ClO_4).—The isoquinolinium bromide (**13**) (3.70 g, 9.74 mmol) in methanol (1.2 l) was irradiated. The reaction mixture was evaporated to dryness and the residue was washed with methanol. The crude product was dissolved in water and 60% aqueous perchloric acid was added to the solution to afford the title compound (1.12 g, 30%). It formed an orange powder from methanol–acetone and methanol–*N*,*N*-dimethylformamide, m.p. > 360 °C (Found: C, 66.9; H, 3.0; N, 3.6. $C_{21}H_{12}ClNO_4$ requires C, 66.8; H, 3.0; N, 3.7%); $\nu_{max.}$(KBr) 3 080, 1 650, 1 315, 1 100, and 860 cm^{-1}; δ(CF_3CO_2H) 7.6—9.4(m).

1-(1-*Naphthylthio*)*isoquinoline*.—A mixture of 1-chloroisoquinoline (6.34 g, 38.8 mmol) and naphthalene-1-thiol (6.83 g, 42.6 mmol) was refluxed in the presence of triethylamine (11.6 g) for 10 h. The mixture was cooled to room temperature, made alkaline by addition of aqueous potassium hydroxide, and extracted with benzene. The extract was washed with water, dried (K_2CO_3), and concentrated to give a grey solid. The solid was recrystallised from benzene to afford the title compound as a white solid (9.11 g, 82%), m.p. 137.3—138.9 °C (corr.) (Found: C, 79.4; H, 4.3; N, 4.7. $C_{19}H_{13}NS$ requires C, 79.4; H, 4.6; N, 4.9%); $\nu_{max.}$(KBr) 3 050, 1 615, 1 550, 1 300, 985, 803, 780, and 742 cm^{-1}; δ($CDCl_3$) 7.1—8.5(m); *m/z* (286 ($M^+ - 1$, 100%) and 287 (M^+, 59%).

2-*Acetonyl*-1-(1-*naphthylthio*)*isoquinolinium Iodide* (**25**).—A mixture of 1-(1-naphthylthio)isoquinoline (2.00 g, 7.0 mmol) and iodoacetone (16.76 g, 91 mmol) was refrigerated for 40 days under a nitrogen atmosphere. Addition of anhydrous benzene (20 ml) to the mixture gave the title compound as a yellow solid (2.46 g, 75%) (Found: C, 56.1; H, 3.6; N, 2.8. $C_{22}H_{18}INOS$ requires C, 56.1; H, 3.9; N, 3.0%); $\nu_{max.}$(KBr) 1 730, 1 620, 1 380, 1 165, 805, and 780 cm^{-1}; δ(CF_3CO_2H) 1.82 (3 H, s, CH_3), 6.01 (2 H, s, CH_2), and 7.0—9.1 (13 H, m, ArH).

4-*Methyl*-2a-*azoniadibenzo*[c,g]*phenanthrene Perchlorate* (**27**: X = ClO_4).—A mixture of the thioisoquinolinium iodide (**25**) (642 mg, 1.36 mmol) and polyphosphoric acid (15 ml) was stirred at 150 °C for 12 h. The mixture was poured onto ice (50 g) and the solution was set aside for 24 h in a refrigerator. The resulting yellowish brown solid was collected and washed with methanol to give a yellow solid (354 mg). The crude thiazepinium salt (**26**) (311 mg) was dissolved in trifluoroacetic acid (6 ml) and the solution filtered to remove an insoluble solid. 30% Hydrogen peroxide (3 ml) was added and the filtrate was set aside for 4 days at room temperature. The colour of the solution changed from reddish yellow to yellow. The mixture was stirred at 80 °C for 3 h. The mixture was cooled and 60% aqueous perchloric acid and water (80 ml) were added to it. The resulting yellow solid was filtered off and washed with water to yield the title compound (**27**; X = ClO_4) (157 mg, 33%), m.p. 257—258 °C) (yellow crystals from methanol–benzene) (Found: C, 66.9; H, 4.0; N, 3.6%. $C_{22}H_{16}ClNO_4$ requires C, 67.1; H, 4.0; N, 3.6%); $\nu_{max.}$(KBr) 1 640, 1 590, 1 400, 1 100, 785, and 760 cm^{-1}; δ(CF_3CO_2H) 2.90 (3 H, s, CH_3) and 7.23—8.63 (13 H, m, ArH).

MO Calculations.—All Hückel MO calculations were carried out with the parameters suggested by Streitwieser, Jr.[16]

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