

Synthesis of Azonia Derivatives of Benzoperylene and Benzocoronene by Photocyclization

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Synopsis. The 2-styrylbenzo[*a*]quinolizinium salt was photocyclized to afford 12a-azoniabenz[*ghi*]perylene salt in 66% yield. The 2a-azoniabenz[*a*]coronene salt was obtained by the photocyclization of 2-[2-(4-biphenyl)vinyl]benzo[*a*]quinolizinium salt and 2-styryl-10-phenylbenzo[*a*]quinolizinium salt in 80% and 75% yields, respectively.

Recently we reported that the photocyclization of *N*-styrylpyridinium-type molecules provided a good route to construct new fused polycyclic azonia aromatic compounds.¹⁾ In these reactions it was demonstrated that the bond formation via a conrotatory photocyclization is possible when the bond order (*Prs*^{*}) between the atoms *r* and *s*, involved in the cyclization in the excited state, has a negative value.¹⁾ Compounds 2-(2-arylvinyl)benzo[*a*]quinolizinium salts (**2**), which was obtained by the reaction of 2-methylbenzo[*a*]quinolizinium salt (**1a**) with benzaldehyde derivatives in the presence of piperidine,^{2,3)} would be an ideal precursor of fused polycyclic azonia aromatic compounds. We report herein the synthesis of azonia derivatives of benzoperylene and benzocoronene by oxidative photocyclization of compounds **2**.

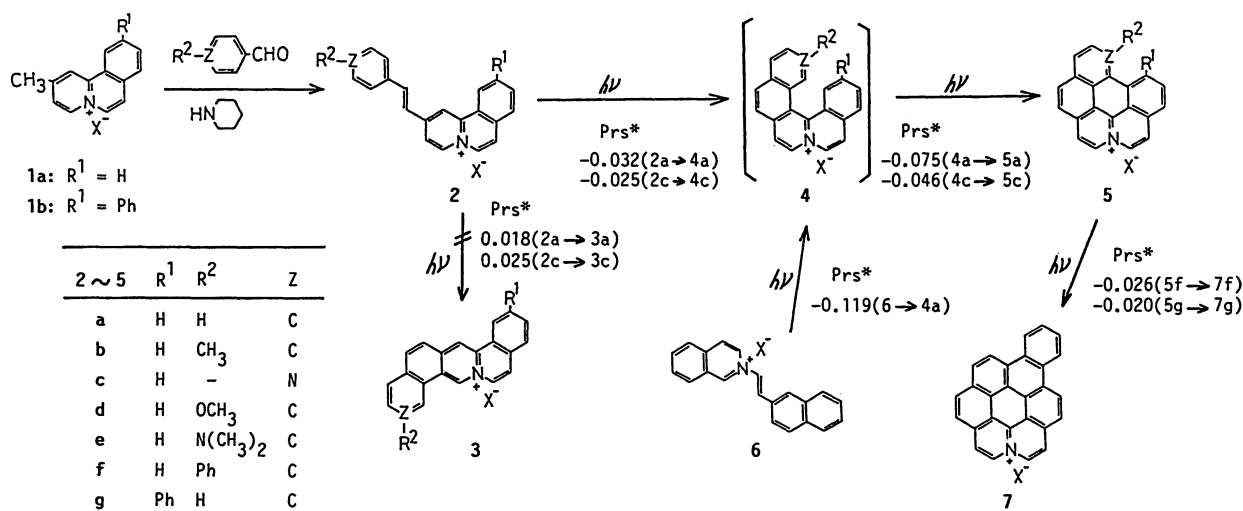
Results and Discussion

The Knoevenagel condensation of 2-methylbenzo[*a*]quinolizinium salt (**1a**) or 2-methyl-10-phenylbenzo[*a*]quinolizinium salt (**1b**) with benzaldehyde derivatives in the presence of piperidine afforded the corresponding *trans*-arylvinyl derivatives **2a—g** in good yields. Compound **2a** was irradiated with a Pyrex-filtered light

($\lambda > 280$ nm) in ethanol in the presence of iodine. The photocyclization of **2a** could, hypothetically, give 6a-azoniadibenzo[*a,h*]anthracene salt (**3a**) and 2a-azoniadibenzo[*c,g*]phenanthrene salt (**4a**). The values of *Prs*^{*}, however, predicted that out of the two possible cyclization products **3a** (*Prs*^{*} = 0.018) and **4a** (*Prs*^{*} = -0.032) only **4a** should be formed. The fast-atom bombardment (FAB) mass spectrum of the isolated product (66% yield) using *m*-nitrobenzyl alcohol as a matrix showed that the ion at highest *m/z* value (278) did not correspond to the intact cation (*C*⁺) of **4a** (*m/z* 280) predicted but to that of 12a-azoniabenz[*ghi*]perylene salt (**5a**) (*C*⁺, *m/z* 278), formed by further photocyclization of **4a**. This structure was confirmed by the fact that the spectral data were identical with those of the photocyclization product¹⁾ of 2-[2-(2-naphthyl)vinyl]isoquinolinium salt (**6**). The *Prs*^{*} value (-0.075) shows that the photocyclization of **4a** is possible to give **5a**.¹⁾ The methyl derivative **2b**³⁾ was also photocyclized to afford 7-methyl-12a-azoniabenz[*ghi*]perylene salt **5b** in 40% yield.

The *Prs*^{*} value predicted that **2c** could be photocyclized by two successive oxidative photocyclization via 9-aza-2a-azoniabenz[*c,g*]phenanthrene salt (**4c**) to afford 7-aza-12a-azoniabenz[*ghi*]perylene salt **5c**. The irradiation of **2c** in ethanol or methanol, however, caused decomposition. Compound **2c** was successfully photocyclized to give **5c** in acetonitrile in 42% yield.

The cyanine-type compounds **2d**²⁾ and **2e**,³⁾ however, failed to undergo photocyclization: the irradiation with or without iodine in ethanol or acetonitrile leads to only



Scheme.

decomposition.

In the photocyclization of **2f**, the values of *Prs** predicted that three successive photocyclizations should take place to give 2a-azoniabenz[*a*]coronene salt (**7**). A methanol solution of **2f** in the presence of iodine was irradiated with a Pyrex-filtered light. The FAB mass spectrum of the product (80% yield) showed the presence of a peak at *m/z* 352 (*C*⁺): this pointed to the loss of six mass units from **2f** (*C*⁺ 358). The FAB mass spectrum of the photocyclization-product (75% yield) from **2g** also exhibited the intact cation at *m/z* 352. The ¹H NMR and UV spectral data of the photoproduct from **2f** was identical with those of the photoproduct from **2g**. These results indicate that photocyclization of both **2f** and **2g** afforded **7** as predicted from *Prs** values.

Experimental

Melting points were determined with a Yamato melting point apparatus (MP21) and are uncorrected. IR spectra were recorded on a JASCO IRA-1 spectrometer. ¹H NMR spectra were recorded on a Hitachi R-24 (60 MHz) or a JEOL FX90Q (90 MHz) spectrometer with Me₄Si as an internal standard. ¹H NMR (400 MHz) and ¹³C NMR (100.40 MHz) spectra were obtained on a JEOL GSX-400 spectrometer. UV spectra were obtained with a Hitachi 220A spectrophotometer. Fast-atom bombardment (FAB) mass spectra were obtained with a JEOL JMS-DX 300 using *m*-nitrobenzyl alcohol as a matrix. Elemental analyses were performed by Mr. Hirokatsu Suzuki at Department of Chemistry, Tokyo Metropolitan University. An Eikosha 300 W high-pressure mercury lamp was used as the irradiation source.

The bond orders (*Prs**) were obtained by Hückel MO calculations using the parameters suggested by Streitwieser, Jr.⁴⁾

2-Methylbenzo[*a*]quinolizinium salt (**1a**) was prepared by photocyclization of 1-styryl-4-methylpyridinium salt according to our previous paper.²⁾ **1a** (X=Br): Found: C, 61.14; H, 4.47; N, 4.99%. **1a** (X=ClO₄): Found: C, 57.23; H, 3.94; N, 4.64%. **1a** (X=PF₆): Found: C, 49.51; H, 3.71; N, 4.15%.

2-Methyl-10-phenylbenzo[*a*]quinolizinium Perchlorate (1b: X=ClO₄): Compound **1b** was prepared in a four-step process according to the method²⁾ described for **1a**. The reaction of 4-methylpyridine with 1-(4-biphenyl)-2-bromoethanone gave 2-(4-methyl-1-pyridinio)-1-(4-biphenyl)ethanone bromide (79% yield): Pale yellow crystals from ethanol; mp 240–242 °C (decomp); ¹H NMR (60 MHz, CF₃CO₂H) δ=2.79 (3H, s, CH₃), 6.32 (2H, s, CH₂), and 7.2–8.7 (13H, m, ArH). Found: C, 64.98; H, 4.81; N, 3.78%. Calcd for C₂₀H₁₈NOBr: C, 65.23; H, 4.98; N, 3.80%.

The pyridinium salt was reduced with NaBH₄ in water to afford 1-[2-hydroxy-2-(4-biphenyl)ethyl]-4-methylpyridinium bromide (54%): Pale yellow crystals from ethanol–benzene; mp 226–228 °C (decomp); ¹H NMR (60 MHz, CF₃CO₂H) δ=2.66 (3H, s, CH₃), 4.7–5.2 (2H, m, CH₂), 5.25–5.6 (1H, m, CH), and 7.2–8.6 (13H, m, ArH). Found: C, 64.94; H, 5.39; N, 3.66%. Calcd for C₂₀H₂₀NOBr: C, 64.87; H, 5.44; N, 3.78%. The reaction between the alcohol with phosphorus tribromide gave 1-[2-(4-biphenyl)vinyl]-4-methylpyridinium bromide (51%): Yellow crystals from 1-pentanol; mp 215–218 °C (decomp); ¹H NMR (60 MHz, CF₃CO₂H) δ=2.56 (3H, s, CH₃) and 7.1–8.8 (15H, m, CH=CH and ArH). Found: C, 68.33; H, 5.30; N, 3.76%. Calcd for C₂₀H₁₈NBr: C, 68.19; H, 5.15; N, 3.98%.

2-Methyl-10-phenylbenzo[*a*]quinolizinium perchlorate (**1b**: X=ClO₄) was obtained by photocyclization of the olefin, followed by anion exchange (33% yield): White crystals from

ethanol–acetonitrile; mp 290–293 °C (decomp); IR (KBr) 1643, 1480, 1312, 1122, 850, and 764 cm⁻¹; ¹H NMR (90 MHz, DMSO-*d*₆) δ=2.81 (3H, s, CH₃) and 7.4–9.7 (15H, m, ArH); FABMS *m/z* 270 (M–ClO₄)⁺. Found: C, 65.23; H, 4.27; N, 3.91%. Calcd for C₂₀H₁₆NClO₄: C, 64.96; H, 4.36; N, 3.79%.

2-(2-Arylviny)benzo[*a*]quinolizinium salts **2a–g** were prepared by the reaction of **1a** or **1b** with benzaldehyde derivatives in the presence of piperidine in methanol, according to our previous paper.^{2,3)}

2-Styrylbenzo[*a*]quinolizinium Hexafluorophosphate (2a: X=PF₆; 69%): Yellowish green crystals from methanol–acetone; mp 239.7–240.5 °C; UV (C₂H₅OH) 401 nm (log ε 4.58); IR (KBr) 3040, 1660, 1640, 1482, 1210, 1162, and 980 cm⁻¹; ¹H NMR (60 MHz, CF₃CO₂H) δ=7.3–9.6 (m, ArH); FABMS *m/z* 282 (M–PF₆)⁺. Found: C, 59.02; H, 3.78; N, 3.28%. Calcd for C₂₁H₁₆NPF₆: C, 59.02; H, 3.89; N, 3.32%.

2-[2-(4-Methylphenyl)vinyl]benzo[*a*]quinolizinium Perchlorate (2b: X=ClO₄ 74%):³⁾ Found: C, 66.55; H, 4.53; N, 3.72%.

2-[2-(4-Pyridyl)vinyl]benzo[*a*]quinolizinium Hexafluorophosphate (2c: X=PF₆; 68%): Yellowish green crystals from methanol; mp 244–247 °C; UV (C₂H₅OH) 388 nm (log ε 4.57); IR (KBr) 3080, 1660, 1640, 1481, and 981 cm⁻¹; ¹H NMR (90 MHz, 7.6–9.7 (m, ArH); FABMS *m/z* 283 (M–PF₆)⁺. Found: C, 55.99; H, 3.56; N, 6.69%. Calcd for C₂₀H₁₅N₂PF₆: C, 56.08; H, 3.54; N, 6.54%.

2-[2-(4-Methoxyphenyl)vinyl]benzo[*a*]quinolizinium Perchlorate (2d: X=ClO₄; 99%):²⁾ Found: C, 64.25; H, 4.30; N, 3.23%.

2-[2-(4-Dimethylaminophenyl)vinyl]benzo[*a*]quinolizinium Bromide (2e: X=Br; 62%):³⁾ Found: C, 68.06; H, 5.34; N, 6.87%.

2-[2-(4-Biphenyl)vinyl]benzo[*a*]quinolizinium Bromide (2f: X=Br; 88%): Yellowish green needles from methanol; mp >300 °C; UV (C₂H₅OH) 272 (log ε 4.41), 290 (4.34), 338 (4.16), 354 (4.29), and 407 nm (4.82); IR (KBr) 1620, 1484, 1195, 1162, 979, and 782 cm⁻¹; ¹H NMR (90 MHz, DMSO-*d*₆) δ=7.4–9.6 (m, ArH); FABMS *m/z* 283 (M–Br)⁺. Found: C, 73.81; H, 4.56; N, 3.23%. Calcd for C₂₇H₂₀NBr: C, 73.98; H, 4.60; N, 3.20%.

2-Styryl-10-phenylbenzo[*a*]quinolizinium Perchlorate (2g: X=ClO₄; 65%): Yellow crystals from methanol; mp 260–263 °C (decomp); UV (CH₃OH) 290 (4.51), 336 (4.30), 348 (4.46), and 410 nm (4.58); IR (KBr) 1618, 1472, 1445, 1120, 975, and 690 cm⁻¹; ¹H NMR (90 MHz, DMSO-*d*₆) δ=7.4–9.7 (m, ArH); FABMS *m/z* 358 (M–ClO₄)⁺. Found: C, 71.06; H, 4.36; N, 3.10%. Calcd for C₂₇H₂₀NClO₄: C, 70.82; H, 4.40; N, 3.06%.

Photocyclization of compounds **2a–g** was carried out according to our previous paper.¹⁾

12a-Azoniabenz[*ghi*]perylene Hexafluorophosphate (5a: X=PF₆; 66%): Yellowish green crystals from methanol–acetone; mp >320 °C; IR (KBr) 1650, 1440, and 1315 cm⁻¹; ¹H NMR (90 MHz, CD₃CN) δ=8.3–9.4 (m, ArH); FABMS *m/z* 278 (M–PF₆)⁺. Found: C, 59.45; H, 2.83; N, 3.50%. Calcd for C₂₁H₁₂NPF₆: C, 59.59; H, 2.86; N, 3.31%.

7-Methyl-12a-azoniabenz[*ghi*]perylene Perchlorate (5b: X=ClO₄; 40%): Pale orange crystals from acetonitrile; mp >300 °C; UV (CH₃OH) 316 (log ε 4.41), 402 (4.09), and 431 nm (4.24); IR (KBr) 1655, 1608, 1404, 1350, 1095, 870, and 742 cm⁻¹; ¹H NMR (90 MHz, DMSO-*d*₆) δ=3.01 (3H, s, CH₃) and 7.9–9.5 (m, 11H, ArH); FABMS *m/z* 292 (M–PF₆)⁺. Found: C, 67.21; H, 3.50; N, 3.37%. Calcd for C₂₂H₁₄NClO₄: C, 67.44; H, 3.60; N, 3.58%.

7-Aza-12a-azoniabenz[*ghi*]perylene Hexafluorophosphate (5c: X=PF₆; 43%): Brown crystals from methanol–acetonitrile; mp >320 °C; UV (C₂H₅OH) 435 (log ε 4.25), 410 (3.99), 388 (3.57), and 373 nm (3.83); IR (KBr) 1640, 1430, and 1340 cm⁻¹; ¹H NMR (90 MHz, CD₃CN) δ=8.4–9.9 (m, ArH);

FABMS m/z 280 ($M-PF_6$)⁺. Found; C, 56.76; H, 2.63; N, 6.59%. Calcd for $C_{20}H_{11}N_2PF_6$; C, 56.62; H, 2.61; N, 6.60%.

2a-Azoniabenz[a]coronene Bromide (7: X=Br; 80%): An orange powder from *N,N*-dimethylformamide-ethanol; mp >300 °C; UV (CH_3OH) 279 (log ϵ 4.46), 339 (4.56), 420 (3.99), and 446 nm (3.98); IR (KBr) 1640, 1342, 856, and 752 cm^{-1} ; 1H NMR (400 MHz, $DMSO-d_6$) δ =7.55 (1H, s, ArH), 7.6–7.7 (3H, m, ArH), 7.87 (1H, s, ArH), 7.9–8.1 (5H, m, ArH), 8.2–8.4 (2H, m, ArH), 8.99 (1H, d, J =4.9 Hz, ArH), and 9.19 (1H, d, J =5.4 Hz, ArH); ^{13}C NMR (100.40 MHz, $DMSO-d_6$) 113.8–133.7 (27 lines); FABMS m/z 352 ($M-Br$)⁺. Found; C, 74.75; H, 3.00; N, 2.98%. Calcd for $C_{27}H_{14}NBr$; C, 75.01; H, 3.26; N, 3.24%.

2a-Azoniabenz[a]coronene Perchlorate (7: X= ClO_4 ; 75%): An orange powder from *N,N*-dimethylformamide-ethanol; mp >300 °C; UV (CH_3OH) 278 (log ϵ 4.45), 338 (4.55), 420 (4.00), and 446 nm (3.99); FABMAS m/z 352 ($M-ClO_4$)⁺. Found; C, 71.50; H, 3.00; N, 2.85%. Calcd for $C_{27}H_{14}NClO_4$;

C, 71.77; H, 3.12; N, 3.10%.

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