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-azoniabenzo[*ghi*]perylene salt in 66% yield. The 2a-azoniabenzo[*a*]coronene salt was obtained by the photocyclization of 2-[2-(4-biphenylyl)vinyl]benzo[*a*]quinolizinium salt and 2-styryl-10-phenylbenzo[*a*]quinolizinium salt in 80% and 75% yields, respectively.

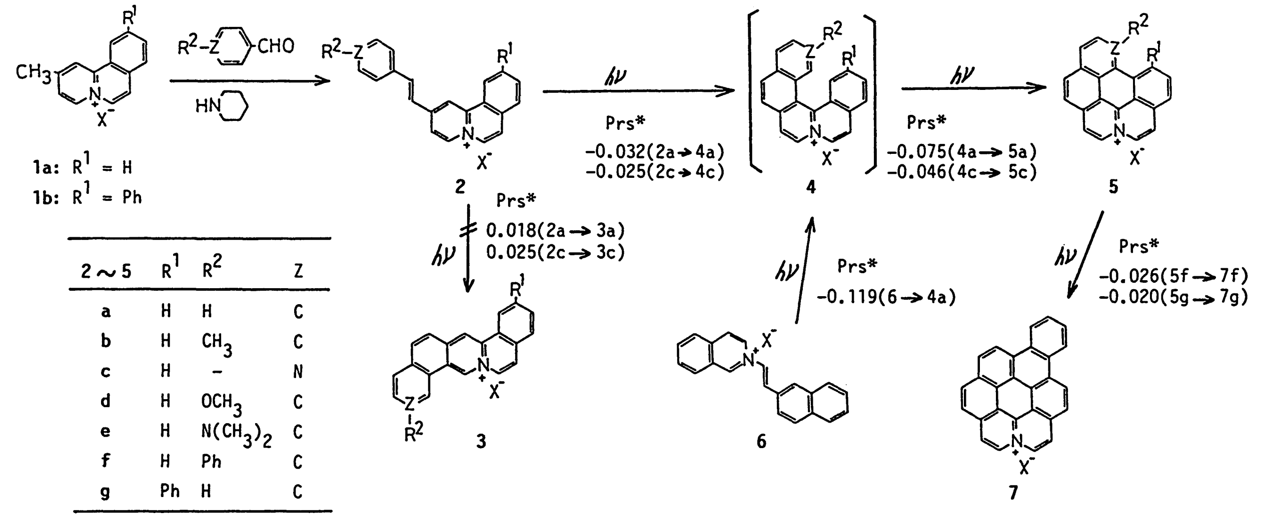
Recently we reported that the photocyclization of *N*-styrylpyridinium-type molecules provided a good route to construct new fused polycyclic azonia aromatic compounds.1) In these reactions it was demonstrated that the bond formation via a conrotatory photocyclization is possible when the bond order (*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 (λ>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-azoniabenzo[*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-azoniabenzo[*ghi*]perylene salt **5b** in 40% yield.

The *Prs** value predicted that **2c** could be photocyclized by two succesive oxidative photocylization via 9-aza-2a-azoniabenzo[*c,g*]phenanthrene salt (**4c**) to afford 7-aza-12a-azoniabenzo[*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



2∼5	R^1	R^2	Z
a	H	H	C
b	H	CH_3	C
c	H	-	N
d	H	OCH_3	C
e	H	$N(CH_3)_2$	C
f	H	Ph	C
g	Ph	H	C

Scheme.

decomposition.

In the photocyclization of **2f**, the values of Prs^* predicted that three succesive photocyclizations should take place to give 2a-azoniabenzo[*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 ^{1}H 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. ^{1}H NMR spectra were recorded on a Hitachi R-24 (60 MHz) or a JEOL FX90Q (90 MHz) spectrometer with Me_4Si as an internal standard. ^{1}H NMR (400 MHz) and ^{13}C 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** ($X=ClO_4$): Found: C, 57.23; H, 3.94; N, 4.64%. **1a** ($X=PF_6$): Found: C, 49.51; H, 3.71; N, 4.15%.

2-Methyl-10-phenylbenzo[*a*]quinolizinium Perchlorate (1b: $X=ClO_4$): Compound **1b** was prepared in a four-step process according to the method[2] described for **1a**. The reaction of 4-methylpyridine with 1-(4-biphenylyl)-2-bromoethanone gave 2-(4-methyl-1-pyridinio)-1-(4-biphenylyl)ethanone bromide (79% yield): Pale yellow crystals from ethanol; mp 240—242 °C (decomp); ^{1}H NMR (60 MHz, CF_3CO_2H) δ=2.79 (3H, s, CH_3), 6.32 (2H, s, CH_2), and 7.2—8.7 (13H, m, ArH). Found: C, 64.98; H, 4.81; N, 3.78%. Calcd for $C_{20}H_{18}NOBr$: C, 65.23; H, 4.98; N, 3.80%.

The pyridinium salt was reduced with $NaBH_4$ in water to afford 1-[2-hydroxy-2-(-4-biphenylyl)ethyl]-4-methylpyridinium bromide (54%): Pale yellow crystals from ethanol–benzene; mp 226—228 °C (decomp); ^{1}H NMR (60 MHz, CF_3CO_2H) δ=2.66(3H, s, CH_3), 4.7—5.2 (2H, m, CH_2), 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 $C_{20}H_{20}NOBr$: C, 64.87; H, 5.44; N, 3.78%. The reaction between the alcohol with phosphorus tribromide gave 1-[2-(4-biphenylyl)vinyl]-4-methylpyridinium bromide (51%): Yellow crystals from 1-pentanol; mp 215—218 °C (decomp); ^{1}H NMR (60 MHz, CF_3CO_2H) δ=2.56 (3H, s, CH_3) and 7.1—8.8 (15H, m, CH=CH and ArH). Found: C, 68.33; H, 5.30; N, 3.76%. Calcd for $C_{20}H_{18}NBr$: C, 68.19; H, 5.15; N, 3.98%.

2-Methyl-10-phenylbenzo[*a*]quinolizinium perchlorate (**1b**: $X=ClO_4$) 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}; ^{1}H NMR (90 MHz, DMSO-d_6) δ=2.81 (3H, s, CH_3) and 7.4—9.7 (15H, m, ArH); FABMS *m*/*z* 270 $(M-ClO_4)^+$. Found; C, 65.23; H, 4.27; N, 3.91%. Calcd for $C_{20}H_{16}NClO_4$; C, 64.96; H, 4.36; N, 3.79%

2-(2-Arylvinyl)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: $X=PF_6$; 69%): Yellowish green crystals from methanol–acetone; mp 239.7—240.5 °C; UV (C_2H_5OH) 401 nm (log ε 4.58); IR (KBr) 3040, 1660, 1640, 1482, 1210, 1162, and 980 cm^{-1}; ^{1}H NMR (60 MHz, CF_3CO_2H) δ=7.3—9.6 (m, ArH); FABMS *m*/*z* 282 $(M-PF_6)^+$. Found: C, 59.02; H, 3.78; N, 3.28%. Calcd for $C_{21}H_{16}NPF_6$: C, 59.02; H, 3.89; N, 3.32%.

2-[2-(4-Methylphenyl)vinyl]benzo[*a*]quinolizinium Perchlorate (2b: $X=ClO_4$ 74%):[3] Found: C, 66.55; H, 4.53; N, 3.72%.

2-[2-(4-Pyridyl)vinyl]benzo[*a*]quinolizinium Hexafluorophosphate (2c: $X=PF_6$; 68%): Yellowish green crystals from methanol; mp 244—247 °C; UV (C_2H_5OH) 388 nm (log ε 4.57); IR (KBr) 3080, 1660, 1640, 1481, and 981 cm^{-1}; ^{1}H NMR (90 MHz, 7.6—9.7 (m, ArH); FABMS *m*/*z* 283 $(M-PF_6)^+$. Found: C, 55.99; H, 3.56; N, 6.69%. Calcd for $C_{20}H_{15}N_2PF_6$: C, 56.08; H, 3.54; N, 6.54%.

2-[2-(4-Methoxyphenyl)vinyl]benzo[*a*]quinolizinium Perchlorate (2d: $X=ClO_4$; 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-Biphenylyl)vinyl]benzo[*a*]quinolizinium Bromide (2f: $X=Br$; 88%): Yellowish green needles from methanol: mp >300 °C; UV (C_2H_5OH) 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}; ^{1}H 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 $C_{27}H_{20}NBr$: C, 73.98; H, 4.60; N, 3.20%.

2-Styryl-10-phenylbenzo[*a*]quinolizinium Perchlorate (2g: $X=ClO_4$; 65%): Yellow crystals from methanol; mp 260—263 °C (decomp); UV (CH_3OH) 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}; ^{1}H NMR (90 MHz, DMSO-d_6) δ=7.4—9.7 (m, ArH); FABMS *m*/*z* 358 $(M-ClO_4)^+$. Found: C, 71.06; H, 4.36; N, 3.10%. Calcd for $C_{27}H_{20}NClO_4$: C, 70.82; H, 4.40; N, 3.06%.

Photocyclization of compounds **2a**—**g** was carried out according to our previous paper.[1]

12a-Azoniabenzo[*ghi*]perylene Hexafluorophosphate (5a: $X=PF_6$; 66%): Yellowish green crystals from methanol–acetone; mp >320 °C; IR (KBr) 1650, 1440, and 1315 cm^{-1}; ^{1}H NMR (90 MHz, CD_3CN) δ=8.3—9.4 (m, ArH); FABMS *m*/*z* 278 $(M-PF_6)^+$. Found; C, 59.45; H, 2.83; N, 3.50%. Calcd for $C_{21}H_{12}NPF_6$: C, 59.59; H, 2.86; N, 3.31%.

7-Methyl-12a-azoniabenzo[*ghi*]perylene Perchlorate (5b: $X=ClO_4$; 40%): Pale orange crystals from acetonitrile; mp >300 °C; UV (CH_3OH) 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}; ^{1}H NMR (90 MHz, DMSO-d_6) δ=3.01 (3H, s, CH_3) and 7.9—9.5 (m, 11H, ArH); FABMS *m*/*z* 292 $(M-PF_6)^+$. Found; C, 67.21; H, 3.50; N, 3.37%. Calcd for $C_{22}H_{14}NClO_4$; C, 67.44 ; H, 3.60; N, 3.58%.

7-Aza-12a-azoniabenzo[*ghi*]perylene Hexafluoroposphate (5c: $X=PF_6$; 43%): Brown crystals from methanol–acetonitrile; mp >320 °C; UV (C_2H_5OH) 435 (log ε 4.25), 410 (3.99), 388 (3.57), and 373 nm (3.83); IR (KBr) 1640, 1430, and 1340 cm^{-1}; ^{1}H NMR (90 MHz, CD_3CN) 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-Azoniabenzo[*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, DMS0-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-Azoniabenzo[*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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