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SYNTHESIS OF 1,2-AZULENEQUINONE DERIVATIVES BY BROMINE-OXIDATION

Hidetsugu Wakabayashi,*[a] Osamu Irinamihira,[a] Satoshi Shibata,[a] Teruo Kurihara,[a] Yuzuru Uchiyama,[b] Akira Ohta,[b] and Kunihide Fujimori[b]

[a]Department of Chemistry, Graduate School of Material Science, Josai University, Sakado, Saitama 350-0295, Japan
[b]Department of Chemistry, Faculty of Science, Shinshu University, Matsumoto, Nagano 390-8621, Japan

Abstract - Treatment of 2-hydroxyazulene (**1a**) with 3 equiv. of $C_5H_5N \cdot HBr_3$ in aqueous THF-AcOH at 0 °C for 1 h afforded 1,1,3-tribromoazulene-2-one (**5a**). 3-Bromo-1,2-azulenequinone (**2a**) was obtained by the hydrolysis of **5a** in the presence of Ag_2O. Annulated compound **6** was readily obtained by the reaction of **2a** with *o*-phenylenediamine.

INTRODUCTION

During the 1980's, Morita, Scott, and Nozoe and co-worker's reported the synthesis of the parent azulenequinones such as 1,5-, 1,7-, and 1,2-azulenequnones and their derivatives.[1-3] Azulenequinones have attracted much attention from the viewpoint of their physicochemical properties and biological activities.[1] Recently, we have reported the preparation of 3-bromo-1,5- and -1,7-azulenequinones and their derivatives in high yields by the one-pot procedure using 4.0-4.5 equiv. molar amount of bromine in aqueous THF-AcOH on azulene.[4] In these synthesis, their azulenequinones may be formed from the hydrolysis of 1,1,3-tribromoazulenium ion obtained by the bromination of azulene. We have also reported the preparation of various alkyl, aryl, alkoxy, and annulated azulene derivatives by the extension of our azulenequinone synthesis method.[4]

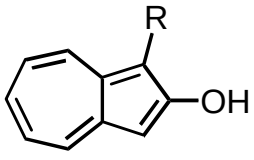
Here, we wish to report a synthetic method for the preparation of 1,2-azulenequinone derivatives from starting materials, 2-hydroxyazulenes (**1a,b**).

Dedicated to Professor Ryoji Noyori on the occasion of his 70 birthday.

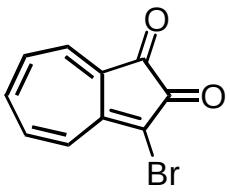
RESULTS AND DISCUSSION

Synthesis of 1,2-azulenequinones

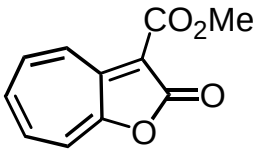
Compound **1a**[5] is obtained in 80% yield by the hydrolysis of 2-methoxyazulene derivative (**4**)[6], obtained by the reaction of 2*H*-cyclohepta[*b*]furan-2-ones (**3**) with orthoacetic acid trimethyl ester, in 75% H_2SO_4 for 1h at 90 °C. Compound **5a** (mp > 300 °C decomp.) was obtained in 94% yield by the treatment of **1a** with pyridinium hydrobromide perbromide ($C_5H_5N \cdot HBr_3$) in THF-AcOH (mole ratio 1:3) for 1 h at 0-2 °C. The MS spectrum of **5a** showed the molecular ion peaks at *m/z* 384, 382, 380, and 378 (rel int. 1:3:3:1). In the ^{1}H NMR spectrum of **5a**, the signals at δ 6.48, 6.72, 6.78, 6.92, and 7.03 can be assigned for H-6, H-7, H-5, H-8, and H-4 on the seven-membered ring, respectively. On the basis of these spectral data, the structure of **5a** was assigned as a 1,1,3-tribromo-2(1*H*)-azulenone. Under the acidic condition such as 100% H_3PO_4 or 75% H_2SO_4 or the basic condition such as NaOMe or morphorin, the expected hydrolysis product, azulenequinone derivatives could not be obtained under these conditions. However, the treatment of **5a** with 100% H_3PO_4 afforded 3-bromo-1,2-azuleneqinone (**2a**) (green needles, mp 129 °C decomp. 73 % yield) in the presence of Ag_2O. Compound **2a** gave molecular ion peaks at *m/z* 236 and 238 (rel. int. 1:1) in EI-MS along with the fragment ion peaks corresponding to the elimination of Br, C=O, and azulenequinone skeleton. Characteristic carbonyl absorptions of azulenequinone in IR spectrum of **2a** were observed at 1747 and 1691 cm^{-1}. In the ^{1}H NMR spectrum of **2a** in $CDCl_3$, the signals at δ 6.23-6.70 can be assigned for the seven-membered ring protons. On the other hand, the ^{1}H NMR spectrum of **2a** in C_6D_6 are shifted upfield by about 1.0 ppm than those in $CDCl_3$.



1a,b **a: R=H**
b: R=CO_2Et



2a



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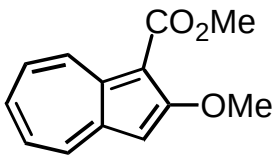

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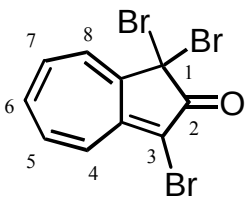
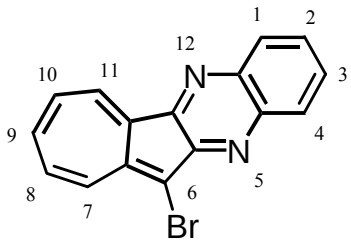


5a



6

The ^{13}C NMR spectrum of **2a** showed two carbonyl carbon at δ 178.45 and 188.20. Therefore, the structure of **2a** was assigned as a 3-bromo-1,2-azulenequinone. Compound **2a** is soluble in chloroform or dichloromethane, but is insoluble in acetone or alcohol. Compound **2a** is also stable in a crystallized condition, but unstable in chloroform solution within 2-3 hs to give an insoluble dark materials.

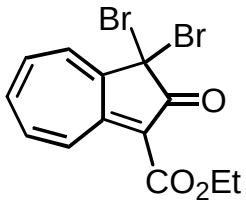
The reaction of 3-bromo-1,5- and -1,7-azulenequinones with the nucleophilic reagents afford various amino, alkoxy, alkylthio derivatives, and heterocyclic annulated derivatives.[4] Thus, we have examined the reaction of **2a** with nucleophilic reagents. For example, the treatment of **2a** with RONa or aliphatic amines afforded complex mixture. However, compound **6** was readily obtained in 87% yield by the reaction of **2a** with *o*-phenylenediamine. The structure of 6-bromoazulene- [1,2-*b*]quinoxaline (**6**) (green needles, mp > 300 °C) was confirmed on the basis of the ^{1}H NMR, ^{13}C NMR, HSQC, and HMBC spectra. From the coupling constants of **6**, the seven-membered ring exhibits bond alternation and proton signals of benzene ring are indicated 4 spin system. The values of the redox potential of **2a** and **6** are summarized in Table 1. These values showed more lower redox potentials than those of the 1,5- and 1,7-azulenequinones.[4]

Table 1. Redox Potentials Measurement of **2a** and **6** in benzonitrile.

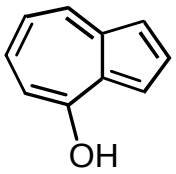
Compounds	E^{ox}	E_1^{red}	E_2^{red}
2a	+1.52*	-0.33	-0.94
6	+1.20*	-0.88	-1.37

*Irreversible

Furthermore, we carried out the reaction of monoester **1b**[5] with bromine under the similar conditions. The resulting compound **5b** (dark red crystals, mp 31-33 °C) was produced in 89% yield. The hydrolysis of **5b** afforded a main product, ethyl 3-bromo-2-hydroxyazulene- 1-carboxylate (**7**) under various reaction conditions, but did not afford the expected ester derivative of 1,2-azulenequinone. The bromine-oxidation of 4- (**8**)[7] and 6-hydroxyazulenes (**9**)[8], synthesized according to the published reports, afforded tribromotropone and its bromo derivatives (**10a-c** and **11a,b**), but did not afford the expected azulenequinones.



5b



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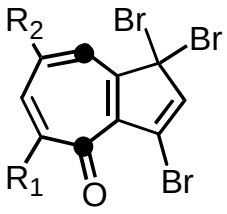
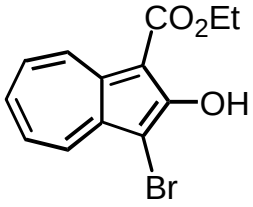


10a-c

a: R_1, R_2=H
b: R_1=Br, R_2=H
c: R_1, R_2=Br



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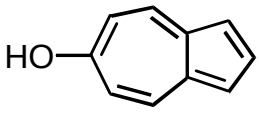

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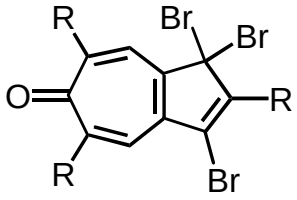

11a,b

a: R=H
b: R=Br

CONCLUSION

1,2-Azulenequinone derivatives **2a** was synthesized from **1a** using our azulenequinone synthetic method by the bromine-oxidation in aqueous THF on azulene. The reactivities of bromine atom of **2a** differ from those of 3-bromo-1,5- and -1,7-azulenequinones. On other hand, monoester **1b** and 4- and 6-hydroxyazulenes afforded the precursor of azulenequinone, but did not afford the expected azulenequinone under similar conditions.

EXPERIMENTAL

Melting points were determined with a Yanagimoto MP-3S melting point apparatus and were uncorrected. The IR and electronic spectra were measured by using a Shimadzu IR-8200PC and a Shimadzu UV-2200 spectrometer, respectively. The NMR spectra were measured with a JEOL ALPHA (500 MHz for ^{1}H and 125.65 MHz for ^{13}C) or a JEOL JNM-EX270 (270 MHz for ^{1}H and 67.8 MHz for ^{13}C) spectrometer using tetramethylsilane as the internal standard; the chemical shifts are expressed in δ values. The assignments of all signals were made by employing decoupling, DEPT, COSY, HSQC, and HMBC techniques. The mass spectra were taken on a JEOL JMSDX300 mass spectrometer and a Shimadzu GCMS-QP5050A spectrometer at 70 eV. TLC was carried out on silica gel Merck 5715 (Kieselgel 60 F254). Silica gel column chromatography were performed on Merck 37563 (Silica gel 60N) and Merck 37560 (Silica gel 60N). Cyclic voltammetry was performed in a three-compartment cell with a Pt disc working electrode, Pt wire counter electrode, and saturated calomel reference electrode (SCE). Measurements were made with a Toho Technical Research Polarization Unit PS-07

potentiostat/galvanostat with a scan rate of 100 mV s^{-1}. The cell contained a solution of a substrate (ca.1 mM) and tetrabutylammonium tetrafluoroborate (0.1 M) as supporting electrolyte in benzonitrile. All solutions were purged with nitrogen and retained under the inert atmosphere during the experiment.

Reaction of 1a with pyridinium hydrobromide perbromide in aqueous THF-AcOH.

To a stirred solution of **1a** (490 mg, 3.40 mmol) in THF (60 mL), water (12 mL), and acetic acid (12 mL) was added $C_5H_5N \cdot HBr_3$ (3.35 g, 10.5 mmol) at 0-2 °C. Upon completion of the addition, the dark brown solution was stirred for 1 h at 0-2 °C. Then, water (60 mL) was added and reaction mixture was stirred overnight at rt. The resulting dark brown solution was evaporated at 30 °C *in vacuo* to remove THF. After cooling, the precipitate was collected by filtration, which was **5a** (1.22 g, 94% yield).

1,1,3-Tribromo-2(1*H*)-azulenone (5a): brown crystals; mp＞300°C (decomp); UV-Vis (in MeOH) λmax (log ε) 260 (4.34), 295 (3.93, sh), 370 (4.23, sh), 395 (4.35), 415 (4.26, sh), 470 (3.43, sh), 510 nm (3.37, sh); IR (KBr) 1686 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.48 (1H, dd, *J* =11.6, 8.4 Hz, H-6), 6.72 (1H, ddd, *J* =11.6, 8.4, 0.5 Hz, H-7), 6.78 (1H, ddd, *J* =11.6, 8.4, 0.5 Hz, H-5), 6.92 (1H, d, *J* =8.4 Hz, H-8), 7.03 (1H, d, *J* =11.6 Hz, H-4); MS (EI, 70 eV): *m/z* (rel intensity) 384 (M^+, 4%), 382 (M^+, 13%), 380 (M^+, 13%), 378 (M^+, 4%)

Synthesis of 3-bromo-1,2-azulenequinone (2a).

A mixture of **5a** (123 mg, 0.32 mmol) and Ag_2O (91 mg, 0.39 mmol) in 100% H_3PO_4 (30 mL) was heated at 85-90 °C for 30 min. After cooling, reaction mixture was neutralized with aqueous $NaHCO_3$ and extracted with $CHCl_3$. The combined extracts were washed with water, dried ($MgSO_4$), and concentrated in vacuo. The residual solid was chromatographed in a column of silica gel with benzene-MeOH (25:1, v/v) and recrystallized from benzene, giving 55 mg (73%) of **2a**: green crystals; mp 129 °C (decomp); UV-Vis (in $CHCl_3$) λmax (log ε) 260 (4.32), 305 (4.02), 335 (4.06, sh), 380 (4.14), 395 (4.09, sh), 460 (3.09), 498 (3.06), 545 (3.02), 585 (2.98), 800 nm (2.65, sh); IR (KBr) 1747, 1691, 1634 cm^{-1}; ^{1}H-NMR (500 MHz, C_6D_6) δ 5.01 (1H, dddd, *J* =11.6, 7.9, 1.0, 0.5 Hz, H-6), 5.13 (1H, ddd, *J* =11.6, 7.8, 0.5 Hz, H-7), 5.16 (1H, ddd, *J* =11.6, 7.9, 0.5 Hz, H-5), 5.47 (1H, dd, *J* =7.8, 1.0 Hz, H-8), 5.86 (1H, dd, *J* =11.6, 0.5 Hz, H-4); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.23 (1H, ddd, *J* =11.0, 8.2, 1.5 Hz, H-6), 6.34 (1H, dd, *J* =7.8, 1.5 Hz, H-8), 6.37 (1H, dd, *J* =11.0, 7.8 Hz, H-7), 6.47 (1H, dd, *J* =11.9, 8.2 Hz, H-5), 6.70 (1H, d, *J* =11.9 Hz, H-4); ^{13}C-NMR (125.65 MHz, $CDCl_3$) δ 116.52 (C-3), 126.07 (C-8), 133.81 (C-7), 135.35 (C-8a), 136.64 (C-5), 137.48 (C-4), 142.16 (C-6), 166.21 (C-3a), 178.45 (C-1), 188.20 (C-2); MS (EI, 70 eV): m/z (rel intensity) 238 (M^+, 24%), 236 (M^+, 23%), 210 (14%), 208 (14%), 182 (15%), 180 (14%), 157 (90%). Anal. Calcd for $C_{10}H_5O_2Br$: C, 50.67; H, 2.13%. Found: C, 50.48; H, 2.52%.

Reaction of 2a with *o*-phenylenediamine in methanol

To a stirred solution of **2a** (66 mg, 0.28 mmol) in MeOH (5 mL) was added *o*-phenylenediamine (39 mg,

0.36 mmol) at rt. After 10 min, the reaction mixture was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (benzene) to give **6** (75 mg, 87% yield).

6-Bromoazuleno[1,2-*b*]quinoxaline (6): green crystals (benzene); mp＞300°C (decomp); UV-Vis (in MeOH) λmax (log ε) 255 (4.12), 262 (4.14), 347 (4.33), 385 (3.65), 407 (3.64), 410 (3.62), 432 (3.74), 460 (3.65), 480 (3.0), 498 (2.8), 525 (2.7), 608 (2.5), 660 nm (2.3); IR (KBr) 2924, 2853, 1638, 1556, 1524, 1508, 748 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.01 (1H, ddd, *J* =11.3, 7.6, 1.5 Hz, H-8), 7.09 (1H, ddd, *J*=11.0, 7.7, 1.5 Hz, H-10), 7.11 (1H, dddd, *J* =11.0, 7.6, 1.5, 0.5 Hz, H-9), 7.84 (1H, ddd, *J* =8.2, 6.7, 1.5 Hz, H-2), 7.87 (1H, dd, *J* =11.3, 0.5 Hz, H-7), 7.91 (1H, ddd, *J* =8.2, 6.7, 1.5 Hz, H-3), 8.38 (1H, dd, *J* =8.2, 1.5 Hz, H-1), 8.46 (1H, dd, *J* =8.2, 1.5 Hz, H-4), 8.47 (1H, dd, *J* =7.7, 1.5 Hz, H-11); ^{13}C-NMR (125.65 MHz, $CDCl_3$) δ 96.12 (C-6), 127.85 (C-2), 128.37 (C-11), 129.30 (C-4), 129.71 (C-10), 129.78 (C-1), 130.12 (C-3), 130.37 (C-8), 133.73 (C-7), 136.29 (C-9), 138.03 (C-11a), 140.29 (C-12a), 143.36 (C-4a), 143.92 (C-6a), 144.73 (C-11b), 149.34 (C-5a); MS (EI, 70 eV): m/z (rel intensity) 310 (M^+, 100%), 308 (M^+, 84%), 229 (36%).

Reaction of 1b with pyridinium hydrobromide perbromide in aqueous THF-AcOH.

To a stirred solution of **1b** (216 mg, 1.00 mmol) in THF (40 mL), water (8 mL), and acetic acid (8 mL) was added $C_5H_5N \cdot HBr_3$ (672 mg, 2.10 mmol) at 0 °C, followed by the same work up procedures as **1a**, giving **5b** (332 mg, 89% yield).

1,1-Dibromo-3-ethoxycarbonyl-2(1*H*)-azulenone (5b): dark red crystals; mp 31-33 °C (decomp.); UV-Vis (MeOH) λmax (log ε) 232 (4.21), 287 (4.20, sh), 298 (4.32), 310 (4.34), 328 (3.90, sh), 355 (3.61), 375 (3.49), 395 (3.30), 490 nm (2.82, sh); IR (KBr) 1734 (C=O) and 1647 cm^{-1} (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.40 (3H, t, *J* =7.0 Hz, CH_3), 4.35 (2H, q, *J* =7.0 Hz, CH_2), 6.89 (1H, dd, *J* =10.8, 8.3 Hz, H-6), 7.09 (1H, dd, *J* =10.8, 8.7 Hz, H-5), 7.14 (1H, dd, *J* =11.6, 8.3 Hz, H-7), 7.52 (1H, d, *J* =8.7 Hz, H-8), 8.54 (1H, d, *J* =11.6 Hz, H-4); MS (EI, 70 eV): m/z (rel intensity) 376 (M^+, 7%), 374 (M^+, 14%), 372 (M^+, 7%), 304 (17%), 302 (33%), 300 (18%), 250 (56%), 248 (50%). Anal. Calcd for $C_{13}H_{10}OBr_2$: C, 41.75; H, 2.69%. Found: C, 42.00; H, 3.03%.

Hydrolysis of 5b in the presence of AgO.

A mixture of **5b** (140 mg, 0.37 mmol) and Ag_2O (100 mg, 0.43 mmol) in 100% H_3PO_4 (30 mL) was heated at 85-90 °C for 30 min, followed by the same work up procedures as **5a**, giving **7** (144 mg, 40% yield).

Ethyl 3-bromo-2-hydroxyazulene-1-carboxylate (7): red crystals; mp 90-91 °C (decomp.); IR (KBr) 3418 (OH) and 1755 cm^{-1} (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.52 (3H, t, *J* =7.0 Hz, CH_3), 4.55 (2H, q, *J* =7.0 Hz, CH_2), 7.54 (1H, t, *J* =9.8 Hz, H-5), 7.55 (1H, t, *J* =9.8 Hz, H-7), 7.62 (1H, t, *J* =9.8 Hz, H-6), 8.31 (1H, d, *J* =9.8 Hz, H-4), 8.96 (1H, d, *J* =9.8 Hz, H-8), 11.07 (1H, s, OH); MS (EI, 70 eV): m/z (rel intensity) 296 (M^+, 18%), 294 (M^+, 18%), 250 (100%), 248 (99%).

Reaction of 4-hydroxyazulene (8)[7] with $C_5H_5N \cdot HBr_3$ in aqueous THF-AcOH.

To a stirred solution of **8** (80 mg, 0.56 mmol) in THF (30 mL), water (6 mL), and acetic acid (6 mL) was added $C_5H_5N \cdot HBr_3$ (538 mg, 1.68 mmol) at 0 °C, followed by the same work up procedures as **1a**, giving a mixture of dark green precipitates **10a-c** (120 mg). The above precipitates was chromatographed on silica gel column with benzene-methanol (25:1, v/v) as eluant, giving **10a** (trace), **10b** (46 mg, 18% yield) and **10c** (30 mg, 10% yield).

10a: FAB-MS m/z 385, 383, 381, 379 (MH^+, 1:3:3:1).

10b: ^{1}H-NMR (500 MHz, C_6D_6) δ 5.65 (1H, dd, *J* =11.0, 9.5 Hz, H-7), 6.55 (1H, dd, *J* =11.0, 1.5 Hz, H-5), 6.57 (1H, s, H-2), 7.25 (1H, dd, *J* =11.0, 1.5 Hz, H-6); FAB-MS m/z 465 , 463, 461, 459, 457 (MH^+, 1:4:6:4:1).

10c: ^{1}H-NMR (500 MHz, C_6D_6) δ 6.99 (1H, d, *J* =1.8 Hz, H-8), 7.16 (1H, s, H-2), 7.76 (1H, d, *J* = 1.8 Hz, H-6); FAB-MS m/z 544, 542, 540, 538, 536, 534 (MH^+, 1:5:10:10:5:1).

Reaction of 6-hydroxyazulene (9)[8] with $C_5H_5N \cdot HBr_3$ in aqueous THF-AcOH.

To a stirred solution of **9** (100 mg, 0.70 mmol) in THF (10 mL), water (6 mL), and acetic acid (2 mL) was added $C_5H_5N \cdot HBr_3$ (670 g, 2.10 mmol) at 0 °C. Upon completion of the addition, the dark brown solution was stirred for 1 h at 0 °C. Then, water (60 mL) was added and the became a yellow solution producing precipitates. After cooling, the precipitate was collected by filtration, which was **11b** (225 g, 52% yield). The above filtrate was extracted with chloroform repeatedly. The extracts was combined, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on silica gel column with benzene-MeOH (25:1, v/v) as eluant, giving **11a** (trace) and its polybromo derivatives.

1,1,3-Tribromo-6(1*H*)-azulenone (11a): yellow solid; FAB-MS m/z 385, 383, 381, 379 (MH^+, 1:3:3:1).

1,1,2,3,5,7-Hexabromo-6(1*H*)-azulenone (11b): yellow solid; IR (KBr) 1608 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.35 (1H, s, H-4 or 8), 8.35 (1H, s, H-8 or 4); ^{13}C-NMR (125.65 MHz, $CDCl_3$) δ 56.21 (C-Br_2), 123.17, 132.83 (CH), 134.85, 135.06 (CH), 136.57, 138.59, 142.20, 146.01, 172.98 (C=O); FAB-MS m/z 624, 622, 620, 618, 616, 614, 612 (MH^+, 1:6:15:20:15:6:1).

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