Journal of the Chinese Chemical Society, **1998**, *45*, 391-400

Synthesis and Reactivities of 1,5- and 1,7-Azulenequinone Derivatives. A Highly Convenient, One-Pot Synthesis of 3-Bromo-1,5- and -1,7-Azulenequinones by Bromination of Azulene[1,2]

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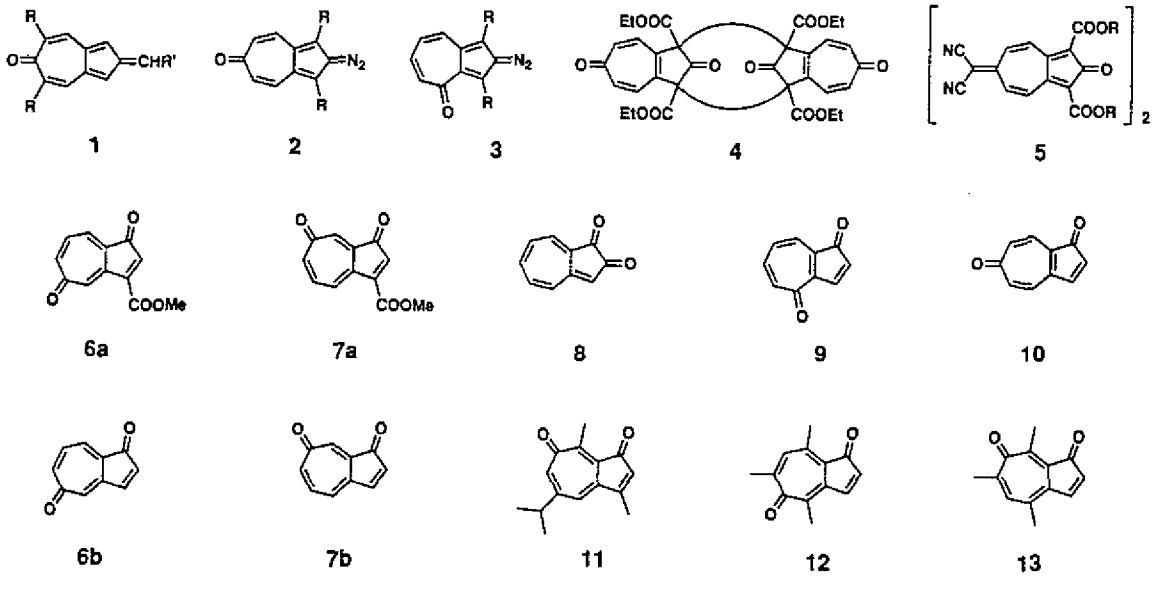
A very convenient, one-pot synthesis (over 80% yield) of 3-bromo-1,5- and -1,7-azulenequinones has been developed by bromination of azulene in aqueous tetrahydrofuran. Reduction of 3-bromo-1,5- and -1,7-azulenequinones with tin or zinc powder in acetic acid gave the parent 1,5- and 1,7-azulenequinones, and further reduction products.

INTRODUCTION

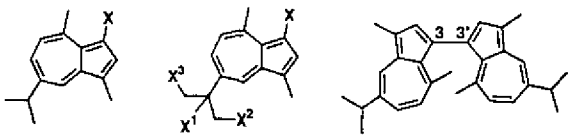
Although quinones are generally believed to constitute one of the oldest and most interesting areas in organic chemistry, almost all of them belong to the benzenoid compounds. As an early study of non-fused azulenequinone analogs, Hafner et al.[3] synthesized several 2-methylene-6(2*H*)-azulenone derivatives (**1**), Nozoe et al.[4] prepared 2-diazo-6(2*H*)- and -4(2*H*)-azulenone derivatives (**2** and **3**; R=CO_2Et or CN), Takase, Morita and their co-workers[5] synthesized diethyl 1,2,3,6-tetrahydro-2,6-dioxoazulene-1,3-dicarboxylate and 6-dicyanomethylene-2,6-dihydro-2-oxoazulene-1,3-dicarboxylate as dimers **4** and **5**, methyl 3,7-dihydro-3,7-dioxoazulene-1-carboxylate (**6a**) and 3,5-dihydro-3,5-dioxoazulene-1-carboxylate (**7a**), and the parent 1,2-azulenequinone (**8**) and its methoxycarbonyl derivatives.

On the other hand, in 1980, Scott, Houk, Fukunaga, Hafner, and their co-workers[6a] published a joint paper on extensive theoretical calculations on all sixteen possible azulenequinones including non-Kekule structures and predicted their various physical properties and stability. They considered that azulenequinones would be the most hopeful candidates for testing their antibiotic, antitumor, and various bio-chemical properties as well as their solid state conductivity. Later, unstable 1,4- and 1,6-azulenequinones (**9** and **10**), and stable 1,5- and 1,7-azulenequinones (**6b** and **7b**) were synthesized.[6b,c]



Almost at the same time, Nozoe, Matsubara, and co-workers[7] obtained guaiazulenequinone (**11**) and 4,6,8-trimethyl-1,5- and -1,7-azulenequinones (**12** and **13**) from the corresponding azulenes by autoxidation or peracetic acid oxidation, but the yields varied according to their respective reaction conditions. The first synthesis of the 1,5- and 1,7-azulenequinones mentioned earlier by Scott et al.[6b,c] is no doubt very important. However, such a multi-step scheme employing diazomethane and a very low temperature (-75 °C) is disadvantageous and not practical. Considerable coincidences of experimental and theoretical calculations suddenly attracted chemists to azulenequinones; however, more practical and general synthetic methods were expected. We now would like to describe our own general and convenient synthesis of 3-bromo-1,5- and -1,7-azulenequinones.

About ten years ago, we started the *N*-bromosuccinimide (NBS) bromination of guaiazulene (**14a**) in benzene, and unexpectedly found that the bromine atom at the C-3 position of 3-bromoguaiazulene (**14b**) shifted both intra- and intermolecularly to the side-chain by radical pathways to give various brominated products (**15**; one or two of X^1-X^3 are Br) and dehydrobrominated products, besides 3,3′-biguaiazulene (**16**), 13,14′-isomers and the parent guaiazulene (**14a**). In methanol **14a** with NBS afforded **14b** (30% yield), **16**, and its 2,3′-isomers (30% yield), trimers and unidentified oligomers.[8] Several products had a methoxy group at C-7 position, but no bromine was found as a substituent of the products. This evidence let us to investigate the bromination of the parent azulene and its derivatives.

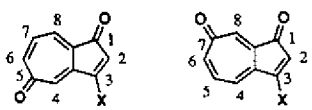


14a,b a: X=H b: X=Br **15** **16**

RESULTS AND DISCUSSION

Synthesis of 3-Bromo-1,5- and -1,7-Azulenequinones by the Bromination of Azulene (19a)

In any common solvents, azulene (**19a**) is easily brominated at C-1 and C-3 positions as expected. The treatment of **19a** with 2 molar amounts of bromine in acetic acid at 10-20 °C afforded 1,3-dibromoazulene (**19b**) as the main product, while 4-5 molar amounts of bromine were added to an acetic acid solution of **19a** at 10-20 °C. Almost all of the substrate was precipitated as a dark green solid, but we were able to isolate it from the mother liquors as a small amount of pale yellow needles of the same molecular formula of $C_{10}H_5O_2Br$, which could be separated by column chromatography. The structures of the two pale yellow needles were determined based on their spectral data. The IR spectra of these two products **17a** and **18a** showed characteristic carbonyl absorption bands at 1710-1700 and 1585-1580 cm^{-1}. The ^1H and ^{13}C NMR spectrum data of **17a** and **18a** are listed in Tables 1 and 2. The assignments of all signals were made by employing decoupling, COSY, HSQC, and HMBC techniques. As we considered that one of the two oxygen atoms in these compounds must originate by the saponification of a gem-dibromo group, we then tried the bromination of **19a** with 5-30% aqueous acetic acid. After optimization, about 50% of a mixture of **17a** and **18a** (3:1 ratio) was obtained together with about 50% of a dark reddish violet solid and small amounts of 3,7-dibromo-1,5- (**20**) and 3,7-dibromo-1,7-azulenequinones (**21**). This solid was separated by alumina column chromatography into a mixture of **24a,b** (15% yield, 1:1 by NMR), **22b** (5% yield), **23b** (5% yield), and an unidentified dark reddish violet solid. The structures of **22b** and **23b** were determined by comparing their spectral data with those of the compounds obtained by the bromination of **22a** and **23a**, formed by the treatment of **17a** and **17b** with **19a**. Further treatment of above dark reddish violet solid with bromine produced another crop of bromo-azulenequinones (30%) with dibromoazulenequinones and related compounds. Therefore, we used slightly more than 4 molar amounts of bromine in 20% aqueous tetrahydrofuran (THF) to avoid precipitation of insufficiently brominated products. Namely, **19a** was treated with 4.3 molar amounts of bromine in 20% aqueous THF containing acetic acid at 0-2 °C for 1 h, after which water was added and stirred overnight at room temperature. The reaction mixtures were dissolved in dichloromethane and chromatographed on alumina gel with dichloromethane as the eluant, giving 3-bromoazulenequinones (**17a** and **18a**, 80% yield, 3:1 ratio) together with a small amount of **20** and **21** (3% yield), and other polybrominated compounds. Addition of water to the above bromination media and immediate separation of the precipitates afforded a 1:1 mixture of tribromoazulenones (**24a,b**), which upon hydrolysis, gave a mixture of **17a** and **18a** in 85% yield. The treatment of 1,3-dibromoazulene[10] (**19b**), obtained by the bromination of

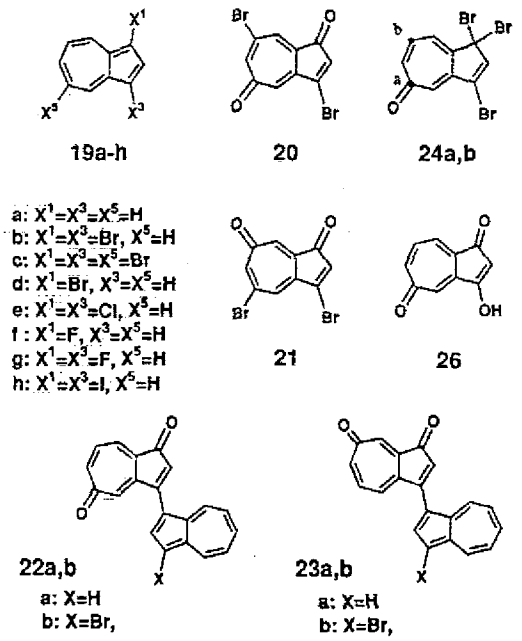


17a-d **18a-d** a: X=Br b: X=Cl c: X=F d: X=I

Table 1. ^{1}H NMR Chemical Shifts for 1,5- and 1,7-Azulenequinone Derivatives

Compounds	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8
1,5-AQ (**6b**)	-	6.56	7.78	6.82	-	6.94	7.11	7.31
3-Br-1,5-AQ (**17a**)	-	6.87	-	7.11	-	7.02	7.17	7.31
3-Cl-1,5-AQ (**17b**)	-	6.87	-	7.14	-	7.01	7.17	7.33
3-I-1,5-AQ (**17d**)	-	7.16	-	6.98	-	7.02	7.17	7.23
1,7-AQ (7b)	-	6.50	7.84	6.76	7.04	6.82	-	7.24
3-Br-1,7-AQ (**18a**)	-	6.81	-	7.05	7.17	6.91	-	7.24
3-Cl-1,7-AQ (**18b**)	-	6.62	-	7.09	7.16	6.92	-	7.27
3-I-1,7-AQ (**18d**)	-	7.10	-	6.90	7.19	6.90	-	7.17

19a, with 2.2 molar amounts of bromine in 20% aqueous THF containing acetic acid at 0-2 °C afforded **17a** and **18a** (70% yield, 3:1 ratio), while the treatment of 1,3,5-tribromoazulene[11] (**19c**), obtained by the NBS bromination of **19a**, with 2.2 molar amounts of bromine under similar conditions, gave dibromoazulenequinones (**20** and **21**) in 25% yield without the formation of **17a** and **18a**.



Pure 3-bromoazulenequinones are stable even after being left standing in air or at the high temperature of 150 °C. However, the treatment of 3-bromoazulenequinones (**17a** and **18a**) with alkali instantly produced a water-soluble brown solid, and after 30 minutes, it precipitated as an insoluble black solid. The ^{1}H NMR spectrum of the product obtained from **17a** with alkali in D_2O was measured in D_2O and consisted of a three spin system with two sets of isolated protons, closely resembling protons of **17a**. Thus, the water-soluble brown solid was proposed to be 3-hydroxy-1,5-azulenequione[9] (**26**).

The possible reaction pathways proposed for the formation of **17a** and **18a** are shown in Scheme I. The electrophilic substitution of **19a** is well known to take place most easily at the C-1 and C-3 positions. As mentioned above, 3-bromoazulenequinones **17a** and **18a** can be obtained from **19b** or **24a,b**. The most favorable first intermediate of the reaction of **19b** with bromine was considered to be 1,1,3-tribromoazulenium bromide **25**, after which the nucleophiles then attack the C-5 or C-7 position to give intermediate **a**. In the case of the bromination of guaiazulene, we recently confirmed the formation of 3-bromoguaiazulenium bromide and 3,3-dibromoguaiazulenium bromide.[12] PM3 calculations[13] have been carried out for the key intermediates **25**

Scheme I

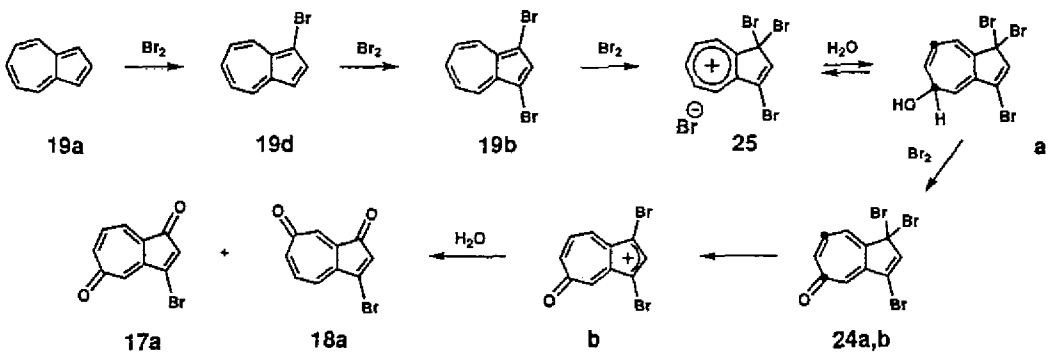
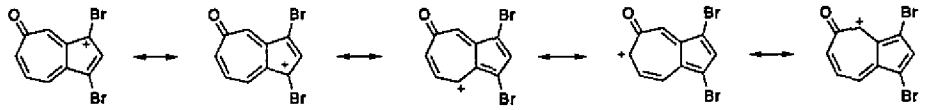


Table 2. ^{13}C NMR Chemical Shifts for 1,5- and 1,7-Azulenequinone Derivatives

Compounds	C-1	C-2	C-3	C-3a	C-4	C-5	C-6	C-7	C-8	C-8a
1,5-AQ (**6b**)	193.92	135.40	154.73	146.25	133.34	187.25	143.92	134.45	128.85	135.64
3-Br-1,5-AQ (**17a**)	189.67	136.47	152.71	144.27	133.59	186.28	144.05	134.46	127.55	134.90
3-Cl-1,5-AQ (**17b**)	189.05	131.81	161.16	143.21	131.59	186.34	144.04	134.50	127.95	136.47
3-I-1,5-AQ (**17d**)	191.03	145.07	130.37	146.42	136.87	186.18	143.99	134.52	126.81	134.01
1,7-AQ (**7b**)	194.77	132.93	155.51	144.42	126.94	135.72	140.26	188.05	134.12	136.47
3-Br-1,7-AQ (**18a**)	190.46	134.07	153.60	142.28	127.19	134.73	141.22	187.40	132.81	135.61
3-Cl-1,7-AQ (**18b**)	189.88	129.63	161.99	141.13	125.29	134.73	141.40	187.41	133.23	136.00
3-I-1,7-AQ (**18d**)	191.72	142.47	131.45	144.62	130.40	134.69	141.03	187.51	132.24	134.65



and **b**. The magnitudes of the π-LUMO coefficients of **25** are in the order of C-5 (-0.482) > C-3a (-0.481) > C-7 (0.425). Aihara's topological resonance energies[14] of $\mathbf{b}_1$-$\mathbf{b}_5$ were calculated to be 0.0646β, 0.0653β, -0.0170β, -0.0257β, and 0.0093β, respectively. The resonance energies of $\mathbf{b}_1$ and $\mathbf{b}_2$ showed large positive values, while the values of $\mathbf{b}_2$, $\mathbf{b}_3$, and $\mathbf{b}_4$ were negative. Therefore, the intermediate **b** is stabilized as a resonance form between $\mathbf{b}_1$ and $\mathbf{b}_2$. The magnitudes of the α-LUMO coefficients of **b** are in the order of C-1 (-0.496) > C-3 (0.429), while the magnitudes of the β-LUMO coefficients are in the order of C-1 (-0.566) > C-3 (0.538). Thus, compound **17a** is produced by the attack of a *hydroxide ion at the C-1 position of intermediate* **b** whereas **18a** is produced by the attack at the C-3 position.

Synthesis of 3-Haloazulenequinones

As 3-bromoazulenequiones (**17a** and **18a**) can be obtained from 1,3-dibromoazulene (**19b**), we then tried to synthesize 3-haloazulenequinones from 1,3-dihaloazulenes. Namely, the treatment of 1,3-dichloroazulene[10] (**19e**), derived from azulene **19a** with *N*-chlorosuccinimide (NCS), with 2 molar amounts of bromine in 20% aqueous THF afforded 3-chloro-1,5- (**17b**, pale yellow needles; mp 140 °C decomp) and -1,7-azulenequinones (**18b**, pale yellow needles; mp 148 °C decomp) in 62% and 21% yields, respectively. The structures of **17b** and **18b** were definitely determined by X-ray crystallographic analysis.[2,15]

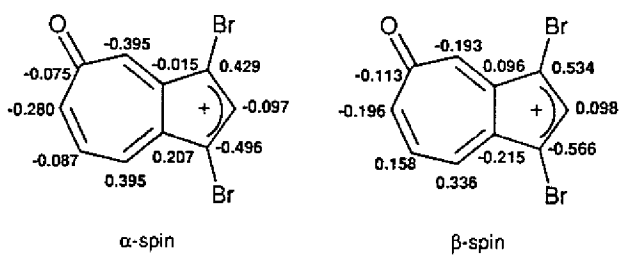


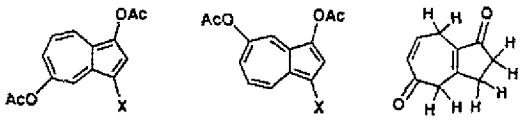
Fig. 1. π-LUMO coefficients of intermediate **b** by UHF/PM3 method.

The treatment of 1-fluoroazulene[16] (**19f**) with bromine afforded **17a** and **18a** in 42% and 33% yields, respectively, but did not give the expected 3-fluoroazulenequinones (**17c** and **18c**). The bromination of 1,3-difluoroazulene[16] (**19g**) under similar conditions confirmed the formation of 3-fluoroazulenequinones (**17c** and **18c**) based on the mass spectral data and after work-up, afforded only 3-hyroxyazulenequinone[9] (**26**). A similar treatment of 1,3-diiodoazulene[17] (**19h**) with bromine afforded a mixture of 3-bromoazulenequinones (**17a** and **18a**) in 64% yields, without the expected 3-iodoazulenequinones (**17d** and **18d**).

The reaction of **17a** or **18a** with excess HCl in THF at room temperature afforded **17b** and **18b**, which easily reverted back to **17a** and **18a** by adding HBr. On the other hand, the reaction of **17a** or **18a** with excess KI in methanol at 40 °C afforded the corresponding 3-iodoazulenequinones (**17d** and **18d**) in 61% and 54% yields, respectively. The ^1H and ^{13}C NMR spectra of the haloazulenequinones are shown in Tables 1 and 2.

Reductive Debromination of 3-Bromo-1,5- and -1,7-Azulenequinone (17a and 18a)

The reductive acetylation of **17a** and **18a** afforded 3-bromodiacetoxyazulenes (**27a** and **28a**) and diacetoxyazulenes (**27b** and **28b**) together with debrominated 2,3,4,8-tetrahydroazulenequinone (**29**) and its isomer. The reductive de-



27a,b 28a,b 29

a: X=Br
b: X=H

bromination of **17a** and **18a** with reducing reagents such as NaH, $LiAlH_4$, $NaBH_4$, and $(n\text{-}Bu)_3SnH$ afforded many products without the formation of the parent azulenequinones **6b** and **7b**. Treatment of **17a** and **18a** with zinc powder in acetic acid at room temperature afforded 2,3,4,8-tetrahydroazulenequinone (**29**) in 44% yield, whereas with tin powder in acetic acid at room temperature for a few minutes, afforded the corresponding parent azulenequinones **6b**[6] and **7b**[6] in 30% yields, respectively. However, when this reaction was continued until the starting material vanished, many products were made, but they did not give the parent azulenequinones. On the other hand, the treatment of 3-iodoazulenequinones (**17d** and **18d**) with copper powder in 5% aqueous nitrobenzene at 120 °C for 10 h afforded the parent 1,5- (**6b**) and 1,7-azulenequinones (**7b**) in 70% and 50% yields, respectively.

EXPERIMENTAL SECTION

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-435 and a Shimadzu UV-2200 spectrometer, respectively. The NMR spectra were measured with a JEOL ALPHA (500 MHz for ^1H and 125.65 MHz for ^{13}C) or a JEOL JNM-EX270 (270 MHz for ^1H 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, COSY, HSQC, and HMBC techniques. The ^1H NMR and ^{13}C NMR spectral data are summarized in Tables 1 and 2. The mass spectra were taken on a JEOL JMSDX300 mass spectrometer and a Shimadzu GCMS-QP2000A spectrometer at 70 eV. TLC was carried out on silica gel (Kieselgel 60 F_{254}). Silica gel and Alumina gel column chromatography were performed on Merck 9385 (Kieselgel 60 F_{254}) and 1067 (Aluminiumoxid 60 aktiv).

Bromination of Azulene (19a)

In 20% aqueous THF solution

To a stirred solution of **19a** (300 mg, 2.3 mmol) in THF (60 mL) and water (12 mL) was added bromine (1.62 g, 10 mmol) in acetic acid (12 mL) at 0-2 °C. Upon completion of the addition, the pale greenish black solution was stirred for 1 h at room temperature. Then, water (60 mL) was added and pale red solution producing white precipitates (**24a,b**) was stirred overnight at room temperature. The resulting dark red solution was evaporated at 40 °C in vacuo to remove THF. The mixture was extracted with dichloromethane (50 mL × 2). The organic layer was washed with water (50 mL × 2) and then saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo. The residual dark red solid (770 mg) was dissolved in dichloromethane (20 mL) and chromatographed on alumina gel with hexane-dichloromethane (4:1, v/v), hexane-dichloromethane (1:1, v/v), and then dichloromethane as eluant, giving 3-bromo-1,5-azulenequinone (**17a**, 322 mg, 58% yield), 3-bromo-1,7-azulenequinone (**18a**, 110 mg, 20% yield), 3,7-dibromo-1,5-azulenequinone (**20**, 14 mg, 2% yield), 3,5-dibromo-1,7-azulenequinone (**21**, 7 mg, 1% yield), and a small amount of other polybrominated compounds.

In 25% aqueous acetic acid solution

To a stirred solution of **19a** (300 mg, 2.3 mmol) in acetic acid (40 mL) and water (14 mL) was added bromine (1.28 g, 8.0 mmol) in acetic acid (2 mL) at 5-10 °C, then water (300 mL). After having been kept at room temperature overnight, the precipitate was collected by filtration, which was **22b** (20 mg, 5% yield), **23b** (21 mg, 5% yield), and a mixture of **24a,b** (135 mg, 15% yield in 1:1 ratio) together with a small amount of unidentified dark reddish violet products. The above filtrate was extracted with dichloromethane, followed by the same work up procedures as above, giving 3-bromo-1,5-azulenequinone (**17a**, 190 mg, 34% yield), 3-bromo-1,7-azulenequinone (**18a**, 88 mg, 16% yield), 3,7-dibromo-1,5-azulenequinone (**20**, < 1%), 3,5-dibromo-1,7-azulenequinone (**21**, < 1%), and other polybrominated compounds.

3-Bromo-1,5-azulenequinone (17a)

Light yellow needles (from EtOAc); mp 135 °C (decomp); UV λ_{max} (MeOH) 254 (log ε 4.16, sh), 264 (4.23), 272 (4.18, sh), 333 (3.68), 348 (3.64), and 387 nm (3.40); IR (KBr) 1700 (s), 1640 (m), 1625 (w), and 1585 cm^{-1} (s); ^1H NMR (270 MHz, $CDCl_3$) δ 6.87 (1H, d, J = 0.7 Hz, H-2), 7.02 (1H, ddd, J = 12.1, 2.4, 1.5 Hz, H-6), 7.11 (1H, dt, J = 2.4, 0.7 Hz, H-4), 7.17 (1H, dd, J = 12.1, 8.0 Hz, H-7), and 7.31 (1H, ddd, J = 8.0, 1.5, 0.7 Hz, H-8); MS (EI, 70 eV): *m/z* (rel intensity) 238 (M^+, 10), 236 (M^+, 10), 210 (15), 208 (15), and 129 (100). Found: C, 50.56; H, 2.23%. Calcd for $C_{10}H_5O_2Br$: C, 50.67; H, 2.13%.

3-Bromo-1,7-azulenequinone (18a)

Pale yellow needles (from EtOAc); mp 142 °C (decomp); UV λ_{max} (MeOH) 238 (log ε 4.21), 245 (4.15, sh), 310 (3.76), 330 (3.68, sh), 372 (3.46), 390 (3.42), and 415 nm (3.18, sh); IR (KBr) 1710 (s), 1640 (m), and 1585 cm^{-1} (s); ^1H NMR (270 MHz, $CDCl_3$) δ 6.81 (1H, s, H-2), 6.91 (1H, ddd, J = 12.2, 2.7, 0.8 Hz, H-6), 7.05 (1H, ddd, J = 8.2, 0.8, 0.5 Hz, H-4), 7.17 (1H, dd, J = 12.2, 8.2 Hz, H-5), and 7.24 (1H, dd, J = 2.7, 0.5 Hz, H-8); MS (EI, 70 eV): *m/z* (rel intensity) 238 (M^+, 11), 236 (M^+, 11), 210 (15), 208 (15), 129 (100), and 101 (50). Found: C, 50.35; H, 2.27%. Calcd for $C_{10}H_5O_2Br$: C, 50.67; H, 2.13%. HRMS Found: *m/z* 237.9447 and 235.9485 (1:1). Calcd for $C_{10}H_5O_2Br$: M, 237.9453 and 237.9473.

3,7-Dibromo-1,5-azulenequinone (20)

Light yellow needles; mp 138 °C (decomp); IR (KBr) 1705 (s), 1635 (m), and 1585 cm^{-1} (s); ^1H NMR (270 MHz, $CDCl_3$) δ 6.89 (1H, d, J = 0.6 Hz, H-2), 7.06 (1H, ddd, J = 2.1, 0.8, 0.6 Hz, H-4), 7.48 (1H, dd, J = 2.3, 0.8 Hz, H-8), and 7.50 (1H, dd, J = 2.3, 2.1 Hz, H-6); MS (EI, 70 eV): *m/z* (rel intensity) 318 (M^+, 5), 316 (M^+, 10), 314 (M^+, 6), 290 (17), 288 (33), 286 (18), 209 (100), and 207 (100). HRMS Found: *m/z* 313.8540, 315.8586, and 317.8555 (1:2:1). Calcd for $C_{10}H_4O_2Br_2$: M, 313.8578, 315.8559, and 317.8539.

3,5-Dibromo-1,7-azulenequinone (21)

Pale yellow needles; mp 153 °C (decomp); IR (KBr) 1705 (s), 1635 (m), and 1590 cm^{-1} (s); ^1H NMR (270 MHz, $CDCl_3$) δ 6.88 (1H, s, H-2), 7.19 (1H, dd, J = 2.6, 0.7 Hz, H-4), 7.25 (1H, dd, J = 2.3, 0.7 Hz, H-8), and 7.42 (1H, dd, J = 2.6, 2.3 Hz, H-6); MS (EI, 70 eV): *m/z* (rel intensity) 318 (M^+, 3), 316 (M^+, 5), 314 (M^+, 3), 290 (20), 288 (40), 286 (21), 209 (96), and 207 (100). HRMS Found: *m/z* 313.8561, 315.8564, and 317.8534 (1:2:1). Calcd for $C_{10}H_4O_2Br_2$: M, 313.8578, 315.8559, and 317.8539.

Synthesis of 1,1,3-Tribromo-5(1*H*)-azulenone (24a) and -7(1*H*)-azulenone (24b)

To a stirred solution of azulene (**19a**, 300 mg, 2.3 mmol) in THF (60 mL) and water (12 mL) was added bromine (1.62 g, 10 mmol) in acetic acid (12 mL) at 0-2 °C. Upon completion of the addition, the pale, greenish black solution was stirred for 1 h at room temperature. Then, water (60 mL) was added and the mixture became a pale, red solution producing white precipitates. After cooling, the precipitate was collected by filtration, which was a mixture of **24a,b** (460 mg, 52% yield). The above filtrate was extracted with chloroform repeatly. The extracts were combined, dried ($MgSO_4$), and evaporated in vacuo. The residue was chromatographed on silica gel column with benzene-MeOH (50:1, v/v) as eluant, giving a mixture of **24a,b** (310 mg, 35% yield): colorless needles (from EtOAc); mp 130 °C (decomp); UV λ_{max} (MeOH) 234 sh, 262 sh, 272, 322, 335, 355 sh, and 370 nm sh; MS (EI, 70 eV): *m/z* (rel intensity) 384 (M^+, 1), 382 (M^+, 2), 380 (M^+, 2), 378 (M^+, 1), 303 (33), 301 (65), 299 (32), 275 (21), 273 (44), 271 (22), and 160 (100). Found: C, 31.80; H, 1.55%. Calcd for $C_{10}H_5OBr_3$: C, 31.54; H, 1.32%. **24a**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.01 (1H, ddd, J = 12.0, 2.4, 1.0 Hz, H-6), 7.07 (1H, ddd, J = 2.4, 0.5, 0.5 Hz, H-4), 7.10 (1H, d, J = 0.5 Hz, H-2), 7.19 (1H, dd, J = 12.0, 8.5 Hz, H-7), and 7.59 (1H, ddd, J = 8.5, 1.0, 0.5 Hz, H-8); ^1H NMR (500 MHz, benzene-d_6) δ 5.96 (1H, dd, J = 12.2, 8.2 Hz, H-7), 6.02 (1H, ddd, J = 8.2, 1.0, 0.5 Hz, H-8), 6.24 (1H, s, H-2), 6.55 (1H, ddd, J = 12.2, 2.6, 1.0 Hz, H-6), and 6.82 (1H, dd, J = 2.6, 0.5 Hz, H-4); **24b**: ^1H NMR (500 MHz, $CDCl_3$) δ 6.97 (1H, ddd, J = 11.9, 2.6, 1.0 Hz, H-6), 7.07 (1H, ddd, J = 8.3, 1.0, 0.5 Hz, H-4), 7.03 (1H, d, J = 0.5 Hz, H-2), 7.21 (1H, dd, J = 11.9, 8.3 Hz, H-5), and 7.68 (1H, dd, J = 2.6, 0.5 Hz, H-8); ^1H NMR (500 MHz, benzene-d_6) δ 5.95 (1H, dd, J = 12.4, 8.2 Hz, H-5), 6.28 (1H, s, H-2), 6.54 (1H, ddd, J = 12.4, 2.6, 1.0 Hz, H-6), 6.85 (1H, ddd, J = 8.2, 1.0, 0.5 Hz, H-4), and 7.76 (1H, dd, J = 2.6, 0.5 Hz, H-8).

Hydrolysis of the Mixture of 1,1,3-Tribromo-5(1*H*)- and -7(1*H*)-Azulenones (24a,b)

A suspension of the mixture of **24a,b** (300 mg, 0.79 mmol) in 50% aqueous THF (100 mL) containing acetic acid (5 mL) was stirred overnight at room temperature, and following the same procedures as described above for **19a**, produced a mixture of **17a** and **18a** (158 mg, 85% yield in 3:1 ratio).

Reaction of 3-Bromo-1,5-azulenequinone (17a) with Azulene (19a)

To a stirred solution of **17a** (100 mg, 0.42 mmol) in acetic acid (12 mL) and water (6 mL) was added **19a** (65 mg, 0.51 mmol) in acetic acid (6 mL) atroom temperature. After standing for 3 days, water (200 mL) was added. The precipitate was collected by filtration, which was **22a** (72 mg, 60% yield), besides the recovered starting material **17a** (15%) from filtrate. Similarly, **23a** (65% yield) was obtained from **18a** and **19a**.

3-(1-Azulenyl)-1,5-azulenequinone (22a)

Reddish brown solid; mp > 300 °C; UV λ_{max} (MeOH) 241 (log ε 4.48), 280 (4.45, sh), 290 (4.49), 350 (4.02), and 495 nm (3.88); IR (KBr) 1690 (s), 1640 (m), 1620 (w), and

1585 cm^{-1} (s); ^1H NMR (270 MHz, $CDCl_3$) δ 6.71 (1H, s, H-2), 7.01 (1H, ddd, J = 11.9, 2.6, 1.5 Hz, H-6), 7.21 (1H, dd, J = 11.9, 7.9 Hz, H-7), 7.27 (1H, d, J = 2.6 Hz, H-4), 7.38-7.46 (3H, m, H-8, 5′,7′), 7.52 (1H, d, J = 4.0 Hz, H-3′), 7.79 (1H, t, J = 9.8 Hz, H-6′), 8.10 (1H, d, J = 4.0 Hz, H-2′), 8.48 (1H, d, J = 9.8 Hz, H-4′), and 8.58 (1H, d, J = 9.8 Hz, H-8′); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 119.41 (CH), 119.94, 126.19 (CH), 126.43 (CH), 127.25 (CH), 130.94 (CH), 133.13 (CH), 135.18 (CH), 136.03 (CH), 137.45 (CH), 138.15, 138.45 (CH), 139.03, 139.66 (CH), 143.50 (CH), 144.20, 147.35, 161.26, 187.33 (C=O), and 192.15 (C=O); MS (EI, 70 eV): *m/z* (rel intensity) 284 (M^+, 100), 255 (75), and 226 (94). Found: C, 84.20; H, 4.48%. Calcd for $C_{20}H_{12}O_2$: C, 84.49; H, 4.25%.

3-(1-Azulenyl)-1,7-azulenequinone (23a)

Reddish brown solid; mp > 300 °C; UV λ_{max} (MeOH) 241 (log ε 4.43), 275 (4.38, sh), 286 (4.40), 345 (3.99), 384 (3.82, sh), and 495 nm (3.80); IR (KBr) 1690 (s), 1640 (w), and 1585 cm^{-1} (s); ^1H NMR (270 MHz, $CDCl_3$) δ 6.67 (1H, s, H-2), 6.90 (1H, ddd, J = 12.2, 2.6, 1.0 Hz, H-6), 7.09 (1H, dd, J = 12.2, 8.2 Hz, H-5), 7.16 (1H, dd, J = 8.2, 1.0 Hz, H-4), 7.39 (1H, d, J = 2.6 Hz, H-8), 7.43 (1H, t, J = 10.0 Hz, H-7′), 7.45 (1H, t, J = 10.0 Hz, H-5′), 7.54 (1H, d, J = 4.0 Hz, H-3′), 7.82 (1H, t, J = 10.0 Hz, H-6′), 8.09 (1H, d, J = 4.0 Hz, H-2′), 8.50 (1H, d, J = 10.0 Hz, H-4′), and 8.61 (1H, d, J = 10.0 Hz, H-8′); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 119.27 (CH), 120.16, 126.23 (CH), 126.23 (CH), 126.46 (CH), 129.13 (CH), 132.93 (CH), 135.45 (CH), 136.18 (CH), 137.02 (CH), 138.51 (CH), 138.94, 138.97, 139.81 (CH), 140.25 (CH), 144.20, 145.50, 162.11, 188.23 (C=O), and 192.75 (C=O); MS (EI, 70 eV): *m/z* (rel intensity) 284 (M^+, 82), 255 (87), and 226 (100). HRMS Found: *m/z* 284.0847. Calcd for $C_{20}H_{12}O_2$: M, 284.0836.

Reaction of 3-(1-azulenyl)-1,5-azulenequinone (22a) with NBS

A mixture of **22a** (80 mg, 0.28 mmol) and NBS (80 mg, 0.45 mmol) in benzene (10 mL) was heated at 40 °C for 8 h. The reaction mixture was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (benzene) to give **22b** (43 mg, 42% yield). Similarly, **23b** (38% yield) was obtained from **23a** and NBS.

3-(3-Bromo-1-azulenyl)-1,5-azulenequinone (22b)

Reddish brown solid; mp > 300 °C; UV λ_{max} (MeOH) 237 (log ε 4.32), 270 (4.32, sh), 283 (4.35), 294 (4.32, sh), 345 (3.86), 502 (3.49), 575 nm (3.06, sh); IR (KBr) 1705 (s), 1645 (m), 1620 (w), and 1595 cm^{-1} (m); ^1H NMR (500 MHz, $CDCl_3$) δ 5.30 (1H, s, H-2), 6.86 (1H, d, J = 2.4 Hz, H-4), 6.99 (1H, ddd, J = 12.2, 2.4, 1.2 Hz, H-6), 7.19 (1H, dd, J = 12.2, 7.9 Hz, H-7), 7.44 (1H, t, J = 9.8 Hz, H-7′), 7.50 (1H, d, J = 7.9 Hz, H-8), 7.57 (1H, t, J = 9.8 Hz, H-5′), 7.88 (1H, tt, J = 9.8, 0.5 Hz, H-6′), 7.99 (1H, s, H-2′), 8.13 (1H, dd, J = 9.8, 0.5 Hz, H-8′), and 8.57 (1H, dd, J = 9.8, 0.5 Hz, H-4′); ^{13}C NMR (125 MHz, $CDCl_3$) δ 106.08, 117.02, 119.56, 126.10 (CH), 126.87 (CH), 128.70 (CH), 130.92 (CH), 132.79 (CH), 134.30 (CH), 136.29, 137.68 (CH), 137.96 (CH), 138.22 (CH), 139.62, 140.83 (CH), 144.07 (CH), 146.28, 162.84, 184.55, and 187.00. Found: C, 65.77; H, 3.13%. Calcd for $C_{20}H_{11}O_2Br$: C, 66.14; H, 3.05%.

3-(3-Bromo-1-azulenyl)-1,7-azulenequinone (23b)

Reddish brown solid; mp > 300 °C; UV λ_{max} (MeOH) 235 (log ε 4.44), 280 (4.28, sh), 292 (4.33), 340 (4.01), 400 (3.66, sh), 500 (3.67), and 570 nm (3.31, sh); IR (KBr) 1700 (s), 1640 (m), and 1590 cm^{-1} (m); ^1H NMR (500 MHz, $CDCl_3$) δ 5.30 (1H, s, H-2), 6.80 (1H, dd, J = 8.2, 0.5 Hz, H-4), 6.87 (1H, ddd, J = 12.3, 2.8, 0.5 Hz, H-6), 7.01 (1H, dd, J = 12.3, 8.2 Hz, H-5), 7.44 (1H, d, J = 2.8 Hz, H-8), 7.47 (1H, t, J = 9.8 Hz, H-7′), 7.58 (1H, t, J = 9.8 Hz, H-5′), 7.90 (1H, tt, J = 9.8, 0.5 Hz, H-6′), 8.00 (1H, s, H-2′), 8.19 (1H, dd, J = 9.8, 0.5 Hz, H-8′), and 8.58 (1H, dd, J = 9.8, 0.5 Hz, H-4′); ^{13}C NMR (125 MHz, $CDCl_3$) δ 105.92, 117.25, 126.12 (CH), 126.30 (CH), 126.89 (CH), 128.33 (CH), 133.85 (CH), 135.36 (CH), 135.91, 136.22, 137.89 (CH), 137.98 (CH), 138.04 (CH), 139.20, 139.98 (CH), 140.95 (CH), 144.35, 158.99, 187.26, and 187.70. Found: C, 65.57; H, 2.95%. Calcd for $C_{20}H_{11}O_2Br$: C, 66.14; H, 3.05%.

Synthesis of 1,3-Dibromoazulene[10] (19b)

To a stirred solution of **19a** (1.10 g, 8.60 mmol) in benzene (80 mL) was added NBS (3.16 g, 17.8 mmol) in benzene (30 mL) at room temperature. After 2 h, the reaction mixture was washed with water (50 mL × 3), dried ($MgSO_4$), and evaporated in vacuo. The residue was chromatographed on silica gel column with benzene as eluant, giving **19b** (2.34 g, 95% yield); ^1H NMR (270 MHz, $CDCl_3$) δ 7.24 (2H, t, J = 9.9 Hz, H-5,7), 7.64 (1H, t, J = 9.9 Hz, H-6), 7.78 (1H, s, H-2), and 8.26 (2H, d, J = 9.9 Hz, H-4,8); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 102.69, 124.01 (CH), 135.74, 136.66 (CH), 138.17 (CH), and 140.02 (CH).

Bromination of 1,3-Dibromoazulene (19b)

To a stirred solution of **19b** (200 mg, 0.70 mmol) in THF (60 mL) and water (12 mL) was added bromine (235 mg, 1.47 mmol) in acetic acid (6 mL) at 0-2 °C. Upon completion of the addition, the pale, greenish black solution was stirred for 1 h at room temperature. Then, water (100 mL)

was added. After being kept at room temperature overnight, the same procedures as in the bromination of **19a** were followed, giving 3-bromo-1,5-azulenequinone (**17a**, 86 mg, 52% yield) and 3-bromo-1,7-azulenequinone (**18a**, 30 mg, 18% yield).

Synthesis of 1,3,5-Tribromoazulene[11] (19c)

A mixture of **19a** (500 mg, 3.9 mmol) and NBS (2.30 g, 13 mmol) in benzene (30 mL) was heated at 50 °C for 4 h, followed by the same work up procedures as **19b**, giving **19c** (830 mg, 58% yield).

1,3,5-Tribromoazulene (19c)

Green needles (from hexane); mp 109-110 °C; ^{1}H NMR (270 MHz, benzene-d_6) δ 6.09 (1H, dd, J = 10.5, 9.8 Hz, H-7), 7.29 (1H, dd, J = 10.5, 2.2 Hz, H-6), 7.36 (1H, s, H-2), 7.73 (1H, d, J = 9.8 Hz, H-8), and 8.43 (1H, d, J = 2.2 Hz, H-4); ^{13}C NMR (67.8 MHz, benzene-d_6) δ 103.76, 104.02, 119.30, 122.83 (CH), 134.14, 135.40 (CH), 136.15, 139.65 (CH), 140.23 (CH), and 142.55 (CH); MS (EI, 70 eV): *m/z* (rel intensity) 368 (M^+, 33), 366 (M^+, 99), 364 (M^+, 100), 362 (M^+, 35), 287 (10), 285 (19), 283 (10), 206 (58), and 204 (60). Found: C, 33.14; H, 1.68%. Calcd for $C_{10}H_5Br_3$: C, 32.92; H, 1.38%.

Bromination of 1,3,5-Tribromoazulene (19c)

To a stirred solution of **19c** (200 mg, 0.55 mmol) in THF (40 mL) and water (8 mL) was added bromine (184 mg, 1.15 mmol) in acetic acid (4 mL) at 0-2 °C, followed by the same work up procedures as bromination of **19a**, giving 3,7-dibromo-1,5-azulenequinone (**20**, 30 mg, 17% yield) and 3,5-dibromo-1,7-azulenequinone (**21**, 15 mg, 9% yield).

Bromination of 1-Fluoroazulene[16] (19f)

To a stirred solution of **19f** (120 mg, 0.82 mmol) in THF (20 mL) and water (5 mL) was added bromine (410 mg, 2.56 mmol) in acetic acid (5 mL) at 0-2 °C. Upon completion of the addition, the greenish black solution was stirred for 1 h at room temperature. Then, water (40 mL) was added. After being kept at room temperature overnight, the same work up procedures as in the bromination of **19a** were followed, giving a mixture of 3-bromo-1,5- (**17a**, 80 mg, 42% yield) and -1,7-azulenequinone (**18a**, 65 mg, 33% yield).

Bromination of 1,3-Difluoroazulene[16] (19g)

To a stirred solution of **19g** (80 mg, 0.49 mmol) in THF (20 mL) and water (5 mL) was added bromine (160 mg, 1.00 mmol) in acetic acid (5 mL) at 0-2 °C for 1 h, then water (40 mL) was added. After being kept at room temperature overnight, the same work up procedures as in the bromination of **19a** were followed, giving a mixture of unstable compound 3-fluoro-1,5- (**17c**) and -1,7-azulenequinones (**18c**).

Synthesis of 1,3-Diiodoazulene[17] (19h)

A mixture of **19a** (500 mg, 3.91 mmol) and NIS (1.93 g, 8.58 mmol) in benzene (50 mL) was heated at 50 °C for 3 h, followed by the same work up procedures as **19b**, giving **19h** (1.42 g, 96% yield); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.33 (2H, t, J = 10.0 Hz, H-5,7), 7.70 (1H, td, J = 10.0, 1.0 Hz, H-6), 8.01 (1H, s, H-2), and 8.19 (2H, dd, J = 10.0, 1.0 Hz, H-4,8); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 74.68, 124.92 (CH), 138.78 (CH), 139.23 (CH), 140.59, and 149.32 (CH).

Bromination of 1,3-Diiodoazulene (19h)

To a stirred solution of **19h** (300 mg, 0.78 mmol) in THF (60 mL) and water (12 mL) was added bromine (265 mg, 1.66 mmol) in acetic acid (12 mL) at 0-2 °C, followed by the same work up procedures as in the bromination of **19a**, giving a mixture of 3-bromo-1,5- and -1,7-azulenequinone (**17a** and **18a**, 120 mg, 64% yield).

Reaction of 3-Chloro-1,5-azulenequinone (17b) with 47% HBr

To a stirred solution of **17b** (20 mg, 0.10 mmol) in THF (10 mL) was added 5 drops of 47% HBr at room temperature. After 2 days, the reaction mixture was neutralized with aqueous $NaHCO_3$, and extracted with benzene. The extracts were combined and concentrated in vacuo. The residue was chromatographed on silica gel column with benzene as eluant, giving **17a** (20 mg, 80% yield). Similarly, **17b** (85% yield) was obtained from **17a** and conc HCl.

Synthesis of 3-Iodo-1,5- (17d) and -1,7-Azulenequinones (18d)

A mixture of **17a** (200 mg, 0.84 mmol) and KI (1.0 g, 6.0 mmol) in 10% aqueous MeOH (70 mL) was heated at 40 °C for 10 h. The solvent was then concentrated in vacuo and the residue extracted with dichloromethane. The extracts were combined and concentrated in vacuo. The residue was chromatographed on alumina gel with hexane-dichloromethane (1:1, v/v) as eluant, giving **17d** (145 mg, 61% yield). Similarly, compound **18d** (54% yield) was obtained from **18a** and KI.

3-Iodo-1,5-azulenequinones (17d)

Light yellow needles (from benzene); mp 158 °C (decomp); UV λ_{max} (MeOH) 220 (log ε 4.07), 241 (3.89), 246

(3.86, sh), 285 (3.70), 315 (3.69), 330 (3.65), 345 (3.33) and 395 nm (3.06, sh); IR (KBr) 1700 (s), 1640 (s), and 1580 cm^{-1} (s); ^1H NMR (500 MHz, $CDCl_3$) δ 6.98 (1H, d, J = 2.7 Hz, H-4), 7.02 (1H, ddd, J = 12.2, 2.7, 1.2 Hz, H-6), 7.16 (1H, s, H-2), 7.17 (1H, dd, J = 12.2, 8.2 Hz, H-7), and 7.23 (1H, dd, J = 8.2, 1.2 Hz, H-8); MS (EI, 70 eV): *m/z* (rel intensity) 284 (M^+, 23), 256 (36), 129 (100), and 101 (68). Found: C, 42.02; H, 2.06%. Calcd for $C_{10}H_5O_2I$: C, 42.28; H, 1.77%.

3-Iodo-1,7-azulenequinones (18d)

Pale yellow needles (from chloroform); mp 160 °C (decomp); UV λ_{max} (MeOH) 220 (log ε 4.32), 245 (4.18, sh), 280 (3.93), 315 (3.95), 328 (3.90, sh), 370 (3.56), 390 (3.53) and 420 nm (3.27, sh); IR (KBr) 1710 (s), 1640 (m), and 1580 cm^{-1} (s); ^1H NMR (500 MHz, $CDCl_3$) δ 6.90 (1H, dd, J = 8.2, 1.0 Hz, H-4), 6.90 (1H, ddd, J = 12.5, 2.6, 1.0 Hz, H-6), 7.10 (1H, s, H-2), 7.17 (1H, d, J = 2.6 Hz, H-8), and 7.19 (1H, dd, J = 12.5, 8.2 Hz, H-5); MS (EI, 70 eV): *m/z* (rel intensity) 284 (M^+, 22), 256 (20), 129 (100), and 101 (60). Found: C, 41.92; H, 2.02%. Calcd for $C_{10}H_5O_2I$: C, 42.28; H, 1.77%.

Reductive Acetylation of 3-Bromo-1,5-azulenequinone (17a) with Zinc-Acetic Anhydride-Pyridine

A mixture of **17a** (70 mg, 0.30 mmol), zinc powder (100 mg, 1.54 mmol), and acetic anhydride (5 mL) in pyridine (2 mL) was stirred at room temperature for 30 min. The reaction mixture was neutralized with dil HCl, and extracted with benzene. The extracts were combined and concentrated in vacuo. The residue was chromatographed on silica gel column with benzene as eluant, giving **27a** (43 mg, 45% yield), **27b**[6] (5 mg, 7% yield), and **29** (5 mg, 10% yield).

1,5-Diacetoxy-3-bromoazulene (27a)

Green needles (from benzene); mp 123 °C (decomp); IR (KBr) 1758 (s) and 1746 cm^{-1} (s); ^1H NMR (270 MHz, benzene-d_6) δ 1.71 (3H, s, $COCH_3$), 1.78 (3H, s, $COCH_3$), 6.42 (1H, dd, J = 10.8, 9.6 Hz, H-7), 7.00 (1H, ddd, J = 10.8, 2.5, 1.2 Hz, H-6), 7.81 (1H, dd, J = 9.6, 1.2 Hz, H-8), 7.93 (1H, s, H-2), and 8.23 (1H, d, J = 2.5 Hz, H-4); MS (EI, 70 eV): *m/z* (rel intensity) 324 (M^+, 8), 322 (M^+, 8), 282 (11), 280 (11), 240 (99), and 238 (100). HRMS Found: *m/z* 323.9824 and 321.9863 (1:1). Calcd for $C_{14}H_{11}O_4Br$: M, 323.9820 and 321.9841.

2,3,4,8-Tetrahydro-1,5-azulenequinone (29)

Colorless needles (from benzene); mp 104-105 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 2.56 (2H, m, H-2), 2.72 (2H, m, H-3), 3.22 (2H, m, J = 6.1, 1.0 Hz, H-8), 3.52 (2H, s, H-4), 5.92 (1H, dt, J = 10.5, 6.1 Hz, H-7), and 6.52 (1H, dt, J = 10.5, 1.0 Hz, H-6); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 31.00 (t, CH_2), 34.89 (t, CH_2), 45.68 (t, CH_2), 48.78 (t, CH_2), 122.36 (d), 124.86 (d), 138.73 (s), 165.06 (s), 203.53 (s, C=O), and 206.31 (s, C=O); MS (EI, 70 eV); *m/z* (rel intensity) 162 (M^+, 96), 133 (81), 105 (37), and 91 (100). Found: C, 73.87; H, 6.02%. Calcd for $C_{10}H_{10}O_2$: C, 74.10; H, 6.20%.

Reductive Acetylation of 3-Bromo-1,7-azulenequinone (18a) with Zinc-Acetic Anhydride-Pyridine

A mixture of **18a** (50 mg, 0.21 mmol), zinc powder (100 mg, 1.54 mmol), and acetic anhydride (5 mL) in pyridine (2 mL) was stirred at room temperature for 30 min, and followed by the same procedures as the described above for **17a**, and produced **28a** (33 mg, 48% yield) and **28b**[6] (5 mg, 10% yield).

1,7-Diacetoxy-3-bromoazulene (28a)

Green needles (from benzene); mp 86-87 °C; IR (KBr) 1758 (s) and 1745 cm^{-1} (s); ^1H NMR (270 MHz, benzene-d_6) δ 1.69 (3H, s, $COCH_3$), 1.74 (3H, s, $COCH_3$), 6.43 (1H, dd, J = 10.7, 9.8 Hz, H-5), 6.94 (1H, ddd, J = 10.7, 2.8, 0.8 Hz, H-6), 7.98 (1H, dd, J = 9.8, 0.8 Hz, H-4), 8.02 (1H, s, H-2), and 8.05 (1H, d, J = 2.8 Hz, H-8); MS (EI, 70 eV): *m/z* (rel intensity) 324 (M^+, 8), 322 (M^+, 8), 282 (11), 280 (11), 240 (99), and 238 (100).

Reduction of 3-Bromo-1,5-azulenequinone (17a) with Zinc

A mixture of **17a** (50 mg, 0.21 mmol) and zinc powder (80 mg, 1.23 mmol) in acetic acid (5 mL) was stirred at room temperature for 10 min, and the reaction mixture was neutralized with aqueous $NaHCO_3$ and extracted with benzene. The extracts were combined and concentrated in vacuo. The residue was chromatographed on silica gel column with benzene-MeOH (50:1, v/v) as eluant, giving **29** (15 mg, 44% yield).

Reduction of 3-Bromoazulenequinones (17a and 18a) with Tin

A mixture of **17a** (50 mg, 0.21 mmol) and tin powder (100 mg, 0.85 mmol) in acetic acid (5 mL) was stirred at room temperature for 10 min, and the reaction mixture was neutralized with aqueous $NaHCO_3$ and extracted with benzene. The extracts were combined and concentrated in vacuo. The residue was chromatographed on alumina gel column with dichloromethane as eluant, giving **6b**[6] (3 mg, 30% yield) and recovered **17a** (70%). Similarly, **7b**[6] (30%

yield) was obtained from **18a** and tin powder.

Reduction of 3-Iodoazulenequinones (17d and 18d) with Copper

A mixture of **17d** (80 mg, 0.28 mmol), Copper powder (0.7 mg, 11 mmol), and water (0.5 mL) in nitrobenzene (15 mL) was heated at 160 °C for 4 h. After reaction, nitrobenezene as solvent was removed by steam distillation. The residual liquid was extracted with benzene, followed by the same work up as the procedures of the reaction mixture with Tin powder, giving **6b** (29 mg, 65% yield). Similarly, **7b** (50% yield) was obtained from **18d** and Copper.

ACKNOWLEDGMENT

We wishes to express our deep gratitude to Professor Klaus Hafner (Technische Hochschule Darmstadt) for his very generous gift of a large amount of azulene. We also thank Mr. Sadaki Yamaguchi for the measurement of the HSQC and HMBC method by NMR spectra, Mr. Hitoshi Fukada for the elemental analysis, Mr. Hideyuki Mitsuhashi for the measurement of the mass spectra (Analytical Center of Josai Univ.), and Mr. Yu-ji Yamamoto, Mr. Kensuke Masaki, and Mr. Michio Okuda for their assistance in some of the experiments.

Received December 5, 1997.

Key Words

Synthesis of 3-bromo-1,5- and 1,7-azulenequinones; 1,5- and 1,7-Azulenequinone; Azulenes; Bromination; One-Pot synthesis.

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