Formation and Structure of 2-Diazo-2,4-azulenequinone Derivatives

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The diazotization of methyl (and ethyl) 2-amino-3-cyano-4-methoxy(and ethoxy)azulene-1-carboxylate (**1**–**4**) was examined to determine whether the products are 2-diazo-2,4-azulenequinone derivatives (**B**) or azulene-2-diazonium-1-carboxylate derivatives (**C**). Since diazotization of **1** and **2** gave the same diazo compound **5** and diazotization of both **3** and **4** gave diazo compound **6**, the diazo compounds are deduced to not be azulene-2-diazonium-1-carboxylate derivatives (**7** and **8**), but rather to be 2-diazo-2,4-azulenequinone derivatives (**5** and **6**). The diazo carbons of both **5** and **6** show ^{13}C NMR signals at δ 66.3, and their carbonyl carbons resonate at δ 181.1, in good agreement with a 2-diazo-2,4-azulenequinone structure. The structures of diazo compounds **24** and **25**, which we have previously reported,[1] are reexamined on the basis of the analysis of their ^{13}C NMR spectra. The contribution of a quinoid structure and a diazoazulenolate structure to **5**, **6**, **24**, and **25** is discussed by comparison of their ^{13}C NMR spectral data with those of 4-diazo-2,5-cyclohexadien-1-one derivatives. It is concluded that the contribution of the quinoid structure is larger than that of the diazoazulenolate structure.

The diazotization of *p*-aminophenol and its derivatives gives the corresponding 4-diazo-2,5-cyclohexadiene-1-one derivatives, which have unusual electronic structures that have been applied as carbene precursors in synthetic organic chemistry, as stabilizers for polymers, and in the development of photolithographic materials[2] (Figure 1).

In contrast, the diazotization of anthranilic acid and its derivatives gives the corresponding benzenediazonium-2-carboxylates, which lose both nitrogen and carbon dioxide when pyrolyzed in certain media and yield benzyne intermediates[3] (Figure 2).

In this paper, we report on the diazotization of methyl (and ethyl) 2-amino-3-cyano-4-methoxy(and ethoxy)azulene-1-carboxylate (**A**). We expected that the products would be either 2-diazo-2,4-azulenequinone derivatives (**B**), which could be carbene precursors of azulene derivatives (**D**), or azulene-2-diazonium-1-carboxylates (**C**), which could be benzyne type precursors of azulene (**E**) (Figure 3).

Prior to the start of this work, we planned to prepare four 2-aminoazulene derivatives of type **A** (**1**–**4**), with the objective of establishing the structure of the diazotization products on the basis of the following (Scheme 1). If the diazotization products were 2-diazo-2,4-azulenequinone derivatives (**B**), compounds **1** and **2** would give the same product **5** and compounds **3** and **4** would both give product **6**.

On the other hand, if the diazotization products were azulene-2-diazonium-1-carboxylates (**C**), compounds **1** and **3** would give the same product **7** and compounds **2** and **4** would both give product **8**.

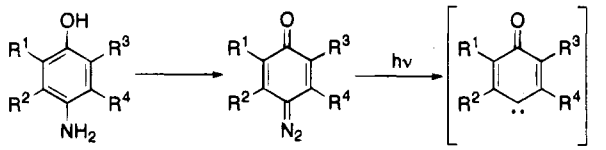

Figure 1.

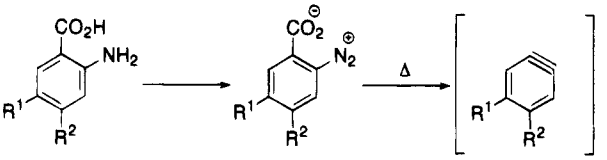

Figure 2.

Results and Discussion

The desired 2-aminoazulene derivatives **1**–**4** were prepared as follows. Treatment of 2-(tosyloxy)tropone (**9**) with dimethyl malonate in the presence of NaOMe in benzene gave methyl 8-hydroxy-2-oxo-2*H*-cyclohepta[*b*]-furan-3-carboxylate (**10**) in 97% yield[4] (Scheme 2). After conversion of **10** to its silver salt (**11**), treatment of the resulting **11** with MeBr or EtBr in refluxing benzene gave the corresponding 8-MeO and 8-EtO derivatives, **12** and **13**, in 61 and 50% yields, respectively. Condensation of **12** and **13** with malononitrile in the presence of NaOMe in benzene gave methyl 2-amino-3-cyano-4-methoxyazulene-1-carboxylate (**1**) and methyl 2-amino-3-cyano-4-ethoxyazulene-1-carboxylate (**2**) in 91 and 88% yields, respectively.

Analogously, **9** gave ethyl 2-amino-3-cyano-4-methoxyazulene-1-carboxylate (**3**) and ethyl 2-amino-3-cyano-4-ethoxyazulene-1-carboxylate (**4**) in 32 and 23% overall yields, respectively (Scheme 3).

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(2) Ershav, V. V.; Nikiforov, G. A.; de Jonge, C. R. *Quinone Diazide*; Elsevier: Amsterdam, 1981.
(3) Stiles, M.; Miller, R. G.; Burchart, U. *J. Am. Chem. Soc.* **1963**, *85*, 1792.
(4) Condensation of 2-[(*p*-tolylsulfonyl)oxy]tropone with ethyl malonate in the presence of NaOEt in ethanol has been reported: Nozoe, T.; Takase, K.; Kato, M.; Nogi, T. *Tetrahedron* **1971**, *27*, 6023.

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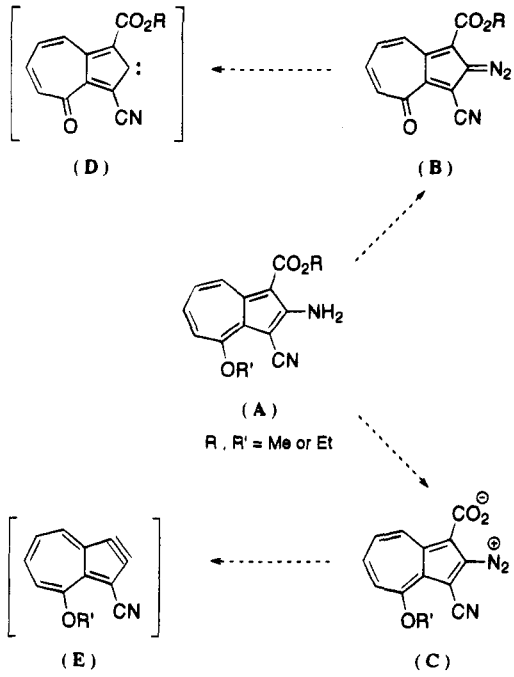
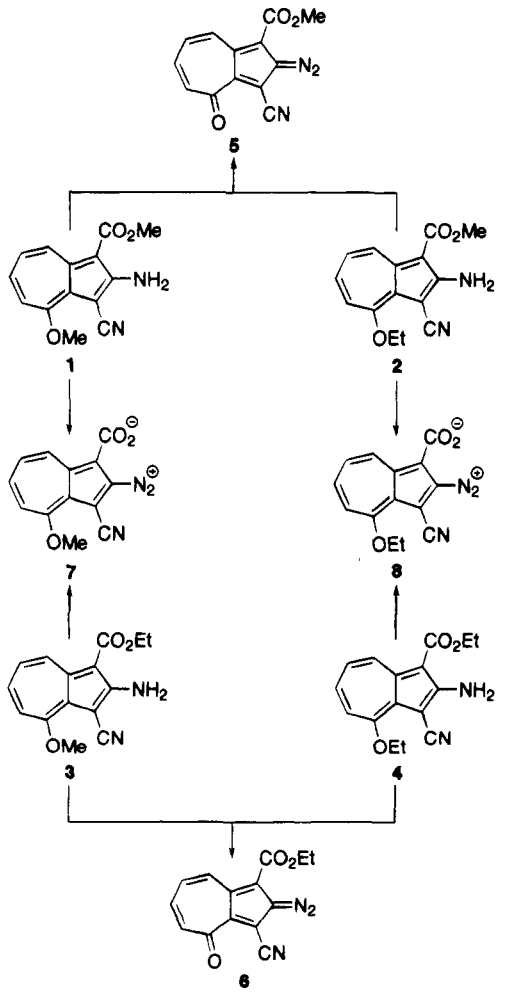


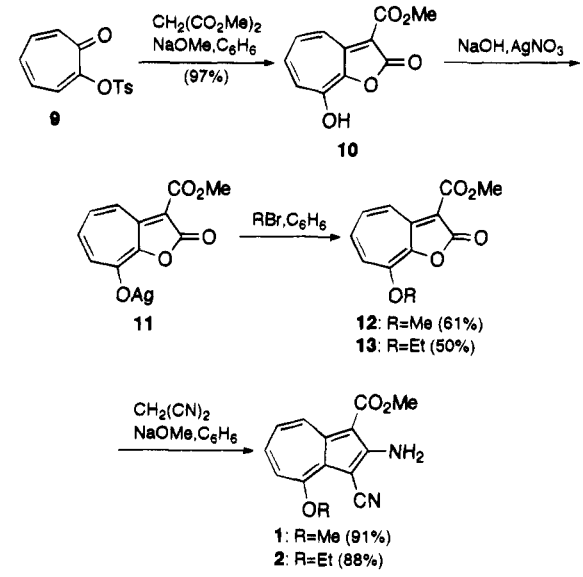
Figure 3.

Scheme 1

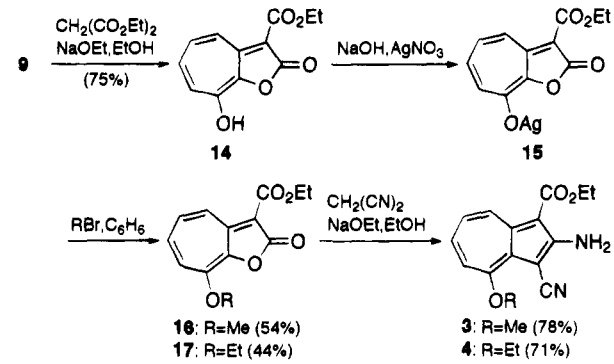


Diazotization of **1** and **2** with sodium nitrite in the presence of concd H_2SO_4 in dioxane gave the same diazo compound (**5**), with a molecular formula of $C_{13}H_7O_3N_3$, in 95 and 97% yields, respectively. The fact that both **1** and **2** gave the same diazo compound (**5**) strongly suggests that the structure of diazo compound **5** is not an azulene-2-diazonium-1-carboxylate derivative but a 2-diazo-2,4-azulenequinone derivative.

Scheme 2



Scheme 3



The 2-diazo-2,4-azulenequinone structure of **5** is supported by the following spectral evidence. Compound **5** showed the absorption band of a diazo group at 2176 cm^{-1} in its IR spectrum. ^{13}C NMR spectra of **5** showed 13 signals in which C-2 bearing the diazo group appeared at δ 66.3 ppm and the C-4 carbonyl carbon appeared at δ 181.1 ppm.

Analogously, diazotization of both **3** and **4** gave diazo compound **6**, with a molecular formula of $C_{14}H_9O_3N_3$, in 92 and 88% yields, respectively. The fact that both **3** and **4** gave the same compound **6**, as well as the IR and ^{13}C NMR evidence, supports a 2-diazo-2,4-azulenequinone structure for **6** by analogy with the above discussion.

The formation of 2-diazo-2,4-azulenequinone derivatives **5** and **6** is reasonably explained by diazotization of the amino group at C-2 of the substrate and successive nucleophilic substitution with water at C-4 of the resulting diazo intermediate (Figure 4).

The structures of **5** and **6** were further confirmed by chemical transformations (Scheme 4). When compounds **5** and **6** were submitted to catalytic hydrogenolysis in the presence of 5% Pd-C and hydrogen at atmospheric pressure, the reaction yielded acidic compounds $C_{13}H_9O_3N$ (**18**) and $C_{14}H_{11}O_3N$ (**19**), respectively, without a change of gas volume. The products **18** and **19** gave methyl ethers **20** and **21** after treatment with diazomethane and

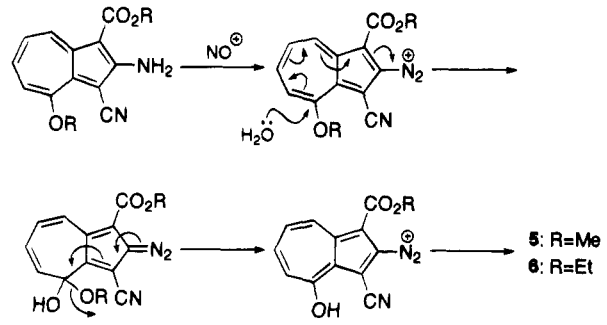
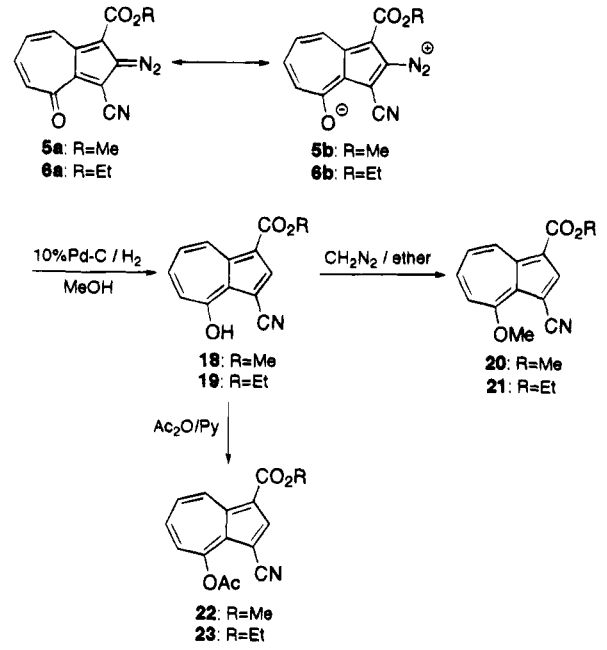


Figure 4.

Scheme 4



acetates **22** and **23** after treatment with acetic anhydride and pyridine, respectively.

As part of our analysis of the ^{13}C NMR spectra, we prepared diethyl 2-diazo-2,6-azulenequinone-1,3-dicarboxylate (**24**) and 2-diazo-1,3-dicyano-2,6-azulenequinone (**25**), as we reported previously[1] (Figure 5).

The ^{13}C NMR chemical shift of diazomethane is δ 23.3, reflecting a partial negative charge at the carbon atom.[5] In contrast, the ^{13}C NMR chemical shift due to the diazo carbon of 9-diazofluorene is δ 63.2 and that of diphenyl diazomethane is δ 62.3, which reflect a partial delocalization of negative charge into the aromatic system.[5] Further, the chemical shifts of C-1 of *p*-benzoquinone and phenol are δ 187.0 and 154.9, respectively.[6] Recently, Sander et al. reported the detailed structure and spectroscopic properties of 4-diazo-2,5-cyclohexadiene-1-one (**26**) and its derivatives.[7] The chemical shift of the diazo carbon of **26** reported by them was δ 73.6 in $CDCl_3$, δ 75.2 in DMSO-d_6, and δ 101.7 in CF_3CO_2D. The large downfield shift of the diazo carbon resonance of **26** in CF_3CO_2D was explained by complete protonation at the oxygen atom in this solvent and delocalization of the negative charge of the diazo carbon at C-4.

The 2-diazo-2,4-azulenequinones (**5** and **6**) which bear methoxycarbonyl or ethoxycarbonyl at C-1 and a cyano

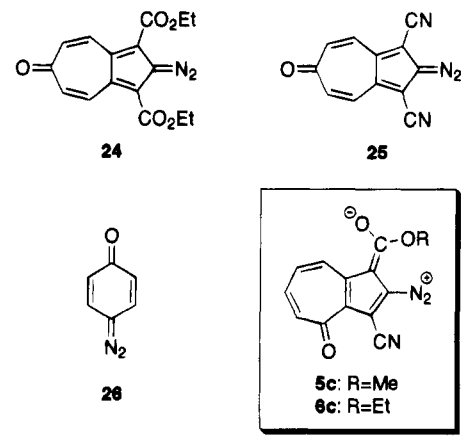


Figure 5.

Table 1. Comparison of ^{13}C NMR Data of 2-Diazo-2,4-azulenequinones 5 and 6 and 2-Diazo-2,6-azulenequinones 24 and 25 with Those of *p*-Quinone Diazide 26

		^{13}C chemical shifts (δ)	
compound	solvent	>C=N2	>C=O
5	DMSO-d_6	66.3	181.1
	CF_3CO_2D	102.9	179.4
6	DMSO-d_6	66.3	181.1
24	$CDCl_3$	85.8	189.5
	CF_3CO_2D	101.9	184.8
25	DMSO-d_6	66.2	187.3
	CF_3CO_2D	103.8	192.2
26	$CDCl_3$	73.6	182.2
	DMSO-d_6	75.2	180.8
	CF_3CO_2D	101.7	173.4

group at C-3 and the 2-diazo-1,3-dicyano-2,6-azulenequinone (**25**) which bears two cyano groups at C-1 and C-3 exhibit diazo carbon (C-2) resonances at δ 66.3, 66.3, and 66.2 in DMSO-d_6, respectively. In contrast, the diazo carbon resonance of diethyl 2-diazo-2,6-azulenequinone-1,3-dicarboxylate (**24**), which bears ethoxycarbonyl groups at C-1 and C-3, appears at δ 85.8 in $CDCl_3$ (Table 1).

The large difference in chemical shift of the diazo carbon (C-2) between **24**, and **5**, **6**, and **25** ($\Delta\delta$ = 19.5 ppm) suggests that the negative charge on C-2 of **24** couples with the carbonyl group on the seven-membered ring or on the substituents at C-1 and C-3 more strongly than in **5**, **6**, and **25**. The C-2 signal in CF_3CO_2D appears at δ 102.9 for **5**, δ 101.9 for **24**, and δ 103.8 for **25**. These δ values are in good agreement with that of *p*-hydroxybenzenediazonium chloride (δ = 102.1 in $CHCl_3$)[5] and clearly show delocalization of C-2 negative charge in **5**, **24**, and **25**, in CF_3CO_2D.

The C-2 and C-4 chemical shifts of 2-diazo-2,4-azulenequinone derivatives are presumed to depend on the negative charge on C-2 and the positive charge on C-4. The diazo carbon resonance of the quinoid form (**5a** and **6a**) must appear at higher field than that of the diazoazulenolate form (**5b** and **6b**) because of the localized negative charge at C-2 in **5a** and **6a**. Conversely, the carbonyl carbon atom of **5a** and **6a** must resonate at a lower field than does that of **5b** and **6b** because of localized positive charge at C-4 in **5a** and **6a**. In another possible resonance structure (**5c** and **6c**), the negative charge on C-2 is delocalized onto the substituents at C-1 and C-3 and the electronic coupling between the diazo group at C-2 and carbonyl group at C-4 is much weaker than in **5b** and **6b**. In this case, the C-2 chemical shift

(5) Duthaler, R. O.; Förster, H. G.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 4974.
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should be to a lower field strength than that of **5a** and **6a**, and the carbonyl carbon atom at C-4 should appear at almost the same position as in quinone form **5a** and **6a**.

The chemical shift of C-4 in **5** and **6** is similar to that of the carbonyl carbon atom (C-1) in **26**, but the chemical shift of C-2 in **5** and **6** appears 8.9 ppm upfield from that of the diazo carbon atom (C-4) in **26**. Obviously, the electronic coupling between the carbonyl and diazo group in **5** and **6** is weaker than it is in **26**.

The diazo carbon resonance of **24** appears 19.5 ppm downfield from those of **5** and **6**, and the carbonyl carbon resonance of **24** also appears 8.4 ppm downfield from those of **5** and **6**. Apparently, the electronic coupling between the carbonyl group at C-6 and the diazo group at C-2 in **24** is weaker than in **5** and **6**, and negative charge on the diazo carbon atom delocalizes onto the ester carbonyl atoms at C-1 and C-3.

The chemical shift of the diazo carbon atom in **25** is very close to that of **5** and **6**, but the C-6 carbonyl carbon atom of **25** appears 6.2 ppm downfield from that of **5** and **6**. Obviously, the electronic coupling between the carbonyl and diazo group in **25** is weaker than in **5** and **6**.

We conclude that the contribution of the quinoid structure is larger than that of the diazoazulenolate structure in 2-diazo-2,4-azulenequinone and 2-diazo-2,6-azulenequinone derivatives.

Experimental Section[8]

Methyl 8-Hydroxy-2-oxo-2*H*-cyclohepta[*b*]furan-3-carboxylate (10). To a stirred mixture of 2-(tosyloxy)tropone (8.28 g, 30 mmol) and dimethyl malonate (7.16 mL, 62.7 mmol) in anhydrous benzene (75 mL) was added NaOMe in MeOH which was prepared from Na (1.38 g, 0.06 g atoms) and absolute MeOH (15 mL). The mixture was stirred at rt for 2.5 h, stored in a refrigerator overnight, poured into a saturated aqueous solution of NaCl, and extracted with benzene. The combined extracts were dried (Na_2SO_4) and concentrated to give methyl 2-oxo-2*H*-cyclohepta[*b*]furan-3-carboxylate (0.15 g, 3%) as yellow needles: mp 157 °C; UV 222 (4.29), 262 (4.30), 406 (4.27) nm; IR 1772, 1692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.95 (3 H, s, CO_2CH_3), 7.27–7.69 (4 H, m), 8.86 (1 H, dd, J = 11.2, 0.7 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 51.6 (q, CO_2CH_3), 96.1 (s, C-8a), 119.3 (d, C-8), 130.6 (d, C-4), 134.1 (d, C-6), 136.1 (d, C-7), 139.6 (d, C-5), 154.5, 158.4 (s, C-3, C-3a), 163.8, 165.1 (s, C-2, CO_2CH_3).

The aqueous layer was acidified by 6 M HCl (25 mL) and allowed to stand at rt overnight. The yellow crystalline material which separated was collected by filtration, washed with water, and dried to give **10** (6.41 g, 97%) as yellow fine needles: mp 241 °C; UV 223 (4.23), 289 (4.28), 356.5 (4.03) nm; IR 3544, 1745, 1718 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.75 (3 H, s, CO_2CH_3), 7.53-7.72 (3 H, m), 8.76 (1 H, dd, J = 10.7, 0.7 Hz, H-4); ^{13}C NMR (DMSO-d_6) δ 50.6 (q, CO_2CH_3), 89.3 (s, C-8a), 130.5 (d, C-4), 131.6 (d, C-7), 134.6 (d, C-6), 136.0 (d, C-5), 143.3 (s, C-8), 150.1, 151.5 (s, C-3, C-3a), 163.9, 164.1 (s, C-2, CO_2CH_3). Anal. Calcd for $C_{11}H_8O_5$: C, 60.00; H, 3.66. Found: C, 59.80; H, 3.87.

(8) All melting points are uncorrected. IR spectra of compounds were measured as KBr disks. ^1H NMR spectra were recorded at 200 MHz and ^{13}C NMR spectra at 50.3 MHz unless otherwise stated. The assignments of ^1H NMR spectra were determined by decoupling and H–H COSY experiments. The assignments of ^{13}C NMR spectra were determined by DEPT and C–H COSY experiments and the measurements of C–H long range coupling constants. UV spectra of compounds were measured as MeOH solutions, and the strength of peak positions is shown in log ϵ in parentheses. Benzene was dried over sodium wire. Dioxane was distilled from sodium metal. MeOH and EtOH were distilled from MeOMg and EtOMg, respectively. Pyridine was distilled from calcium hydride and stored over 4 Å sieves. Reactions were run under 1 atm of nitrogen.

Methyl 8-Methoxy-2-oxo-2*H*-cyclohepta[*b*]furan-3-carboxylate (12). To a stirred solution of the Na salt of **10** which was formed from a suspension of **10** (1.89 g, 8.58 mmol) in H_2O (80 mL) and 1 M NaOH (7.2 mL) was added a solution of silver nitrate (1.77 g, 10.4 mmol) in H_2O (12 mL). After the solution was stirred for 30 min, the mixture was allowed to stand at rt overnight, and the precipitates were collected by filtration under reduced pressure and dried in a dessicator overnight and then at 65–70 °C under reduced pressure for 1.5 h to give a silver salt (**11**) (1.74 g). The mixture of **11** and MeI (741 μL, 11.9 mmol) in anhydrous benzene (20 mL) was refluxed under stirring for 8 h. The reaction mixture was extracted with benzene by a Soxhlet extractor and concentrated to give **12** (1.22 g, 61%) as an orange-colored crystals: mp 207 °C; UV 225 (4.21), 296.5 (4.25), 392.5 (4.12) nm; IR 1770, 1678 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.93 (3 H, s, CO_2CH_3), 4.19 (3 H, s, OCH_3), 7.35–7.58 (3 H, m), 9.02 (1 H, d, J = 11.5 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 51.5 (q, CO_2CH_3), 58.5 (q, OCH_3), 92.1 (s, C-8a), 126.5 (d, C-7), 132.4 (d, C-4), 133.4 (d, C-6), 135.4 (d, C-5), 146.5 (s, C-8), 150.6, 152.1 (s, C-3, C-3a), 164.6, 164.9 (s, C-2, CO_2CH_3). Anal. Calcd for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 61.74; H, 4.29.

Methyl 8-Ethoxy-2-oxo-2*H*-cyclohepta[*b*]furan-3-carboxylate (13). By the analogous method for the preparation of **12**, **10** (2.80 g, 12.7 mmol) was transformed into **13** (1.57 g, 50%) as yellow needles: mp 159 °C; UV 225.5 (4.41), 297.5 (4.46), 392.0 (4.33) nm; IR 1758, 1686 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53 (3 H, t, J = 7.0 Hz, OCH_2CH_3), 3.93 (3 H, s, CO_2CH_3), 4.46 (2 H, q, J = 7.0 Hz, OCH_2CH_3), 7.27–7.56 (3 H, m), 9.02 (1 H, dd, J = 11.6, 1.2 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 15.0 (q, OCH_2CH_3), 51.4 (q, CO_2CH_3), 67.7 (t, OCH_2CH_3), 92.1 (s, C-8a), 127.7 (d, C-7), 132.3 (d, C-4), 133.5 (d, C-6), 135.5 (d, C-5), 146.6 (s, C-8), 150.4, 152.0 (s, C-3, C-3a), 164.6, 165.1 (s, C-2, CO_2CH_3). Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 62.93; H, 4.96.

Methyl 2-Amino-3-cyano-4-methoxyazulene-1-carboxylate (1). To a stirred mixture of **12** (984 mg, 4.2 mmol) and malonitrile (555 mg, 8.4 mmol) in absolute MeOH (20 mL) cooled at 0 °C in an ice bath was added NaOMe which was prepared from Na (193 mg, 0.0084 g atoms) and absolute MeOH (8.4 mL). After stirring was continued for 2 h at this temperature, the reaction mixture was allowed to stand at rt overnight and poured into water (80 mL). The mixture was stored in a refrigerator for 2 h and filtered to give **1** (984 mg, 91%) as an orange-colored crystalline material: mp 221 °C; UV 244 (4.56), 323 (4.67), 360 (3.86), 393 (3.86), 455.5 (3.58) nm; IR 3456, 3340, 2204, 1660 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.88 (3 H, s, CO_2CH_3), 4.13 (3 H, s, OCH_3), 7.31 (2 H, br s, NH_2), 7.39–7.66 (3 H, m), 9.03 (1 H, d, J = 9.6 Hz, H-8); ^{13}C NMR (DMSO-d_6) δ 50.7 (q, CO_2CH_3), 56.7 (q, OCH_3), 80.9 (s, CN), 97.2 (s, C-2), 116.2 (d, C-5), 117.1 (s), 127.7 (d, C-7), 132.3 (d, C-8), 132.9 (d, C-6), 134.6 (s), 140.9 (s), 158.8 (s), 159.5 (s), 165.3 (s, CO_2CH_3). Anal. Calcd for $C_{14}H_{12}O_3N_2$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.85; H, 4.83; N, 10.87.

Methyl 2-Amino-3-cyano-4-ethoxyazulene-1-carboxylate (2). To a stirred mixture of **13** (745 mg, 3.0 mmol) and malononitrile (396 mg, 6.0 mmol) in absolute MeOH (15 mL) cooled at 0 °C in an ice bath was added NaOMe which was prepared from Na (138 mg, 0.006 g atoms) and absolute MeOH (6 mL). The mixture was treated by the method for the preparation of **1** to give **2** (717 mg, 88%) as orange-colored crystals: mp 208 °C; UV 244 (4.60), 323 (4.67), 360.5 (3.87), 391 (3.87), 456 (3.58) nm; IR 3444, 3328, 2204, 1660 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.52 (3 H, t, J = 7.0 Hz, OCH_2CH_3), 3.87 (3 H, s, CO_2CH_3), 4.42 (2 H, q, J = 7.0 Hz, OCH_2CH_3), 7.29 (2 H, br s, NH_2), 7.39–7.64 (3 H, m), 9.03 (1 H, d, J = 9.5 Hz, H-8); ^{13}C NMR (DMSO-d_6) δ 13.8 (q, OCH_2CH_3), 50.7 (q, CO_2CH_3), 65.8 (t, OCH_2CH_3), 81.0 (s, CN), 97.2 (s, C-2), 116.8 (d, C-5), 117.1 (s), 127.6 (d, C-7), 132.3 (d, C-8), 132.9 (d, C-6), 134.4 (s), 140.9 (s), 158.3 (s), 159.6 (s), 165.3 (s, CO_2CH_3). Anal. Calcd for $C_{15}H_{14}O_3N_2$: C, 66.65; H, 5.22; N, 10.37. Found: C, 66.46; H, 4.74; N, 9.95.

Ethyl 8-Hydroxy-2-oxo-2*H*-cyclohepta[*b*]furan-3-carboxylate (14). To a stirred mixture of 2-(tosyloxy)tropone (8.28 g, 30 mmol) and diethyl malonate (9.49 mL, 62.7 mmol) in absolute EtOH (62 mL) cooled in an ice bath at 0 °C was

added NaOEt which was prepared from Na (1.38 g, 0.06 g atoms) and absolute EtOH (60 mL). The mixture was stirred at rt for 0.5 h, stored in a refrigerator overnight, poured into a saturated aqueous solution of NaCl, and extracted with benzene.

The benzene extracts gave ethyl 2-oxo-2*H*-cyclohepta[*b*]-furan-3-carboxylate (1.26 g, 19%) as orange-colored crystals: mp 133 °C; UV 222.5 (4.39), 261.5 (4.42), 4.05 (4.39) nm; IR 1772, 1694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (3 H, t, J = 7.1 Hz, $CO_2CH_2CH_3$), 4.42 (2 H, q, J = 7.1 Hz, $CO_2CH_2CH_3$), 7.32–7.71 (4 H, m), 8.82 (1 H, d, J = 11.3 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 14.5 (q, $CO_2CH_2CH_3$), 60.6 (t, $CO_2CH_2CH_3$), 96.6 (s, C-8a), 119.3 (d, C-8), 130.7 (d, C-4), 134.1 (d, C-6), 136.2 (d, C-7), 139.6 (d, C-5), 154.4, 158.5 (s, C-3, C-3a), 163.4, 165.2 (s, C-2, $CO_2CH_2CH_3$). Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.30; H, 4.70.

The aqueous layer was acidified by 6 M HCl (16 mL) and allowed to stand at rt overnight to give **14** (5.27 g, 75%) as yellow needles: mp 187 °C; UV 224.5 (4.25), 289.5 (4.34), 357 (4.10) nm; IR 3484, 1724, 1670 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.32 (3 H, t, J = 7.1 Hz, $CO_2CH_2CH_3$), 4.26 (2 H, q, J = 7.1 Hz, $CO_2CH_2CH_3$), 7.48–7.69 (3 H, m), 8.75 (1 H, d, J = 10.5 Hz, H-4); ^{13}C NMR (DMSO-d_6) δ 14.4 (q, $CO_2CH_2CH_3$), 59.1 (t, $CO_2CH_2CH_3$), 89.6 (s, C-8a), 130.5 (d, C-4), 131.6 (d, C-7), 134.5 (d, C-6), 135.9 (d, C-5), 143.2 (s, C-8), 150.2, 151.3 (s, C-3, C-3a), 163.5, 164.1 (s, C-2, $CO_2CH_2CH_3$). Anal. Calcd for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 61.41; H, 4.24.

Ethyl 8-Methoxy-2-oxo-2*H*-cyclohepta[*b*]furan-3-carboxylate (16). Compound **16** was prepared from **14** by the method for the preparation of **12** in 54% yield as yellow needles: mp 144 °C; UV 225 (4.42), 297 (4.47), 392.5 (4.34) nm; IR 1770, 1674 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (3 H, t, J = 7.1 Hz, $CO_2CH_2CH_3$), 4.18 (3 H, s, OCH_3), 4.41 (2 H, q, J = 7.1 Hz, $CO_2CH_2CH_3$), 7.30–7.50 (3 H, m), 9.01 (1 H, dd, J = 11.5, 1.4 Hz, C_4-H); ^{13}C NMR ($CDCl_3$) δ 14.6 (q, $CO_2CH_2CH_3$), 58.3 (q, OCH_3), 60.3 (t, $CO_2CH_2CH_3$), 92.3 (s, C-8a), 126.3 (d, C-7), 132.4 (d, C-4), 133.5 (d, C-6), 135.3 (d, C-5), 146.3 (s, C-8), 150.5, 151.8 (s, C-3, C-3a), 164.2, 164.8 (s, C-2, $CO_2CH_2CH_3$). Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 63.01; H, 4.90.

Ethyl 8-Ethoxy-2-oxo-2*H*-cyclohepta[*b*]furan-3-carboxylate (17). Compound **17** was prepared from **14** by the method for the preparation of **13** in 44% yield as yellow needles: mp 136 °C; UV 225 (4.39), 297.5 (4.43), 392.5 (4.30) nm; IR 1746, 1678 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (3 H, t, J = 7.1 Hz, $CO_2CH_2CH_3$), 1.53 (3 H, t, J = 7.0 Hz, OCH_2CH_3), 4.41 (2 H, q, J = 7.1 Hz, $CO_2CH_2CH_3$), 4.45 (2 H, q, J = 7.0 Hz, OCH_2CH_3), 7.30–7.53 (3 H, m), 8.99 (1 H, dd, J = 11.6, 1.2 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 14.5 (q, $CO_2CH_2CH_3$), 14.9 (q, OCH_2CH_3), 60.1 (t, $CO_2CH_2CH_3$), 67.5 (t, OCH_2CH_3), 92.3 (s, C-8a), 127.4 (d, C-7), 132.1 (d, C-4), 133.2 (d, C-6), 135.2 (d, C-5), 146.4 (s, C-8), 150.0, 151.7 (s, C-3, C-3a), 164.1, 164.9 (s, C-2, $CO_2CH_2CH_3$).

Ethyl 2-Amino-3-cyano-4-methoxyazulene-1-carboxylate (3). To a stirred mixture of **16** (273 mg, 1.1 mmol) and malononitrile (145 mg, 2.2 mmol) in absolute EtOH (6 mL) cooled at 0 °C in an ice bath was added NaOEt which was prepared from Na (51 mg, 0.0022 g atoms) and absolute EtOH (2.2 mL). The mixture was treated by the method for the preparation of **1** and **2** to give **3** (231 mg, 78%) as a yellow crystalline material: mp 182 °C; UV 244 (4.73), 323 (4.80), 359 (3.99), 393 (3.99), 456.5 (3.70) nm; IR 3460, 3340, 2204, 1662 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.39 (3 H, t, J = 7.1 Hz, $CO_2CH_2CH_3$), 4.14 (3 H, s, OCH_3), 4.38 (2 H, q, J = 7.1 Hz, $CO_2CH_2CH_3$), 7.30 (2 H, br s, NH_2), 7.39–7.70 (3 H, m), 9.05 (1 H, d, J = 9.9 Hz, H-8); ^{13}C NMR (DMSO-d_6) δ 14.4 (q, $CO_2CH_2CH_3$), 56.7 (q, OCH_3), 59.4 (t, $CO_2CH_2CH_3$), 80.9 (s, CN), 97.3 (s, C-2), 116.2 (d, C-5), 117.1 (s), 127.7 (d, C-7), 132.4 (d, C-8), 132.9 (d, C-6), 134.6 (s), 140.9 (s), 158.8 (s), 159.7 (s), 165.0 (s, $CO_2CH_2CH_3$). Anal. Calcd for $C_{15}H_{14}O_3N_2$: C, 66.65; H, 5.22; N, 10.37. Found: C, 66.23; H, 5.14; N, 10.09.

Ethyl 2-Amino-3-cyano-4-ethoxyazulene-1-carboxylate (4). Compound **4** was prepared from **17** by the method for the preparation of **3** in 71% yield as orange-colored crystals; mp 194 °C; UV 244.5 (4.61), 324 (4.67), 392.5 (3.87), 455 (3.68) nm; IR 3440, 3320, 2208, 1654 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.37 (3 H, t, J = 7.1 Hz, $CO_2CH_2CH_3$), 1.52 (3 H, t, J = 7.0 Hz, OCH_2CH_3), 4.37 (2 H, q, J = 7.1 Hz, $CO_2CH_2CH_3$), 4.43 (2 H, q, J = 7.0 Hz, OCH_2CH_3), 7.27 (2 H, br s, NH_2), 7.40–7.65 (3 H, m), 9.06 (1 H, d, J = 9.9 Hz, H-8); ^{13}C NMR (DMSO-d_6) δ 13.8 (q, $CO_2CH_2CH_3$), 14.4 (q, OCH_2CH_3), 59.3 (t, $CO_2CH_2CH_3$), 65.8 (t, OCH_2CH_3), 81.0 (s, CN), 97.3 (s, C-2), 116.8 (d, C-5), 117.1 (s), 127.6 (d, C-7), 132.4 (d, C-8), 132.9 (d, C-6), 134.4 (s), 140.8 (s), 158.3 (s), 159.6 (s), 165.0 (s, $CO_2CH_2CH_3$).

Methyl 3-Cyano-2-diazo-2,4-azulenequinone-1-carboxylate (5). To a stirred solution of **1** (514 mg, 2.0 mmol) in dioxane (20 mL) and concd H_2SO_4 (1.3 mL) cooled in an ice bath was added $NaNO_2$ (166 mg, 2.4 mmol) in water (1 mL) over 15 min. The mixture was stirred for 1.5 h, poured into water (50 mL), and filtered to give **5** (490 mg, 97%) as orange-colored crystals: mp 170 °C dec; UV 243.5 (4.43), 279 (4.17), 308 (4.29), 437 (3.61) nm; IR 2224, 2176, 1724 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ 3.93 (3 H, s, CO_2CH_3), 6.67 (1 H, d, J = 12.3 Hz, H-5), 6.77 (1 H, dd, J = 11.6, 8.4 Hz, H-7), 7.18 (1 H, dd, J = 12.3, 8.4 Hz, H-6), 8.18 (1 H, d, J = 11.6 Hz, H-8); ^1H NMR ($CDCl_3$) δ 4.01 (3 H, s, CO_2CH_3), 6.66 (1 H, ddd, J = 11.5, 8.4, 1.0 Hz, H-7), 6.77 (1 H, d, J = 12.3 Hz, H-5), 7.03 (1 H, ddd, J = 12.3, 8.4, 1.0 Hz, H-6), 8.20 (1 H, d, J = 11.5 Hz, H-8); ^{13}C NMR (150 MHz, DMSO-d_6) δ 52.4 (q, CO_2CH_3), 66.3 (s, C-2), 103.3 (s, CN), 113.3 (s, C-3), 117.9 (s, C-1), 126.1 (d, C-7), 130.2 (s, C-8a), 130.4 (d, C-8), 133.6 (d, C-5), 136.2 (s, C-3a), 136.7 (d, C-6), 161.0 (s, CO_2CH_3), 181.1 (s, C-4). Anal. Calcd for $C_{13}H_7O_3N_3$: C, 61.64; H, 2.79; N, 16.60. Found: C, 61.74; H, 2.90; N, 16.19.

Diazotization of 2. Diazotization of **2** with $NaNO_2$ and concd H_2SO_4 in dioxane under the same reaction conditions as above gave **5** in 95% yield.

Ethyl 3-Cyano-2-diazo-2,4-azulenequinone-1-carboxylate (6). Diazotization of **3** under the same reaction conditions as above gave **6** in 92% yield as orange-colored crystals: mp 162 °C dec; UV 244 (4.54), 308 (4.43), 437.5 (3.57) nm; IR 2220, 2168, 1684 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.36 (3 H, t, J = 7.1 Hz, $CO_2CH_2CH_3$), 4.39 (2 H, q, J = 7.1 Hz, $CO_2CH_2CH_3$), 6.67 (1 H, d, J = 12.3 Hz, H-5), 6.77 (1 H, dd, J = 11.6, 8.4 Hz, H-7), 7.18 (1 H, dd, J = 12.3, 8.4 Hz, H-6), 8.19 (1 H, dd, J = 11.6, 0.8 Hz, H-8); ^1H NMR ($CDCl_3$) δ 1.45 (3 H, t, J = 7.1 Hz, $CO_2CH_2CH_3$), 4.46 (2 H, q, J = 7.1 Hz, $CO_2CH_2CH_3$), 6.64 (1 H, ddd, J = 11.7, 8.3, 0.9 Hz, H-7), 6.74 (1 H, dd, J = 12.4, 0.9 Hz, H-5), 7.27 (1 H, ddd, J = 12.4, 8.3, 0.8 Hz, H-6), 8.19 (1 H, dd, J = 11.7, 0.8 Hz, H-8); ^{13}C NMR (DMSO-d_6) δ 13.7 (q, $CO_2CH_2CH_3$), 61.5 (t, $CO_2CH_2CH_3$), 66.3 (s, C-2), 103.2 (s, CN), 113.3 (s, C-3), 117.9 (s, C-1), 126.1 (d, C-7), 130.2 (s, C-8a), 130.3 (d, C-8), 133.5 (d, C-5), 136.2 (s, C-3a), 136.7 (d, C-6), 160.5 (s, $CO_2CH_2CH_3$), 181.1 (s, C-4). Anal. Calcd for $C_{14}H_9O_3N_3$: C, 62.92; H, 3.39; N, 15.73. Found: C, 62.91; H, 3.45; N, 15.51.

Diazotization of 4. Diazotization of **4** with $NaNO_2$ and concd H_2SO_4 in dioxane under the same reaction conditions as above gave **6** in 88% yield.

Methyl 3-Cyano-4-hydroxyazulene-1-carboxylate (18). A mixture of **5** (304 mg, 1.2 mmol) and 10% Pd-C (100 mg) in MeOH (100 mL) was stirred under a H_2 atmosphere for 30 min, filtered through Celite, concentrated, and recrystallized from MeOH to give **18** (220 mg, 81%) as orange crystals: mp 216–220 °C dec; UV 242.5 (4.55), 279.5 (4.18), 310.5 (4.36), 434.0 (3.51) nm; IR 3444, 2216, 1700 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ 3.85 (3 H, s, CO_2CH_3), 7.51 (1 H, d, J = 11.3 Hz, H-5), 7.51 (1 H, dd, J = 10.5, 9.9 Hz, H-7), 7.99 (1 H, dd, J = 11.3, 9.9 Hz, H-6), 8.17 (1 H, s, H-2), 9.44 (1 H, d, J = 10.5 Hz, H-8); ^{13}C NMR (150 MHz, DMSO-d_6) δ 51.1 (q, CO_2CH_3), 92.7 (s, CN), 115.9 (s, C-1), 118.5 (s, C-3), 121.7 (d, C-5), 125.7 (d, C-7), 130.4 (s, C-3a), 138.1 (s, C-8a), 138.1 (d, C-8), 138.8 (d, C-2), 141.0 (d, C-6), 164.1 (s, CO_2CH_3), 167.6 (s, C-4). Anal. Calcd for $C_{13}H_9O_3N$: C, 68.72; H, 3.99; N, 6.17. Found: C, 67.84; H, 4.33; N, 6.12.

Ethyl 3-Cyano-4-hydroxyazulene-1-carboxylate (19). Hydrogenolysis of **6** under the same reaction conditions as for the preparation of **18** from **5** gave **19** in 75% yield as orange crystals: mp 208 °C dec; UV 244.5 (4.62), 311 (4.38), 439.5 (3.48) nm; IR 3456, 2220, 1698 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.36 (3 H, t, J = 7.1 Hz, $CO_2CH_2CH_3$), 4.32 (2 H, q, J = 7.1 Hz, $CO_2CH_2CH_3$), 7.517 (1 H, dd, J = 10.0, 9.8 Hz, H-7), 7.523

(1 H, d, J = 11.5 Hz, H-5), 8.00 (1 H, ddd, J = 11.5, 10.0, 1.0 Hz, H-6), 8.18 (1 H, s, H-2), 9.45 (1 H, d, J = 9.8 Hz, H-8); ^{13}C NMR (DMSO-d_6) δ 14.3 (q, $CO_2CH_2CH_3$), 59.6 (t, $CO_2CH_2CH_3$), 92.6 (s, *C*N), 116.3 (s, C-1), 118.4 (s, C-3), 121.5 (d, C-5), 125.7 (d, C-7), 130.3 (s, C-3a), 138.2 (d, C-8), 138.2 (s, C-8a), 138.9 (d, C-2), 141.0 (d, C-6), 163.6 (s, $CO_2CH_2CH_3$), 167.3 (s, C-4). Anal. Calcd for $C_{14}H_{11}O_3N$: C, 69.70; H, 4.59; N, 5.80. Found: C, 69.68; H, 4.67; N, 5.87.

Methyl 3-Cyano-4-methoxyazulene-1-carboxylate (20). Methylation of **18** (45 mg, 0.20 mmol) with CH_2N_2 (0.40 mmol/723 μL of ether) in ether (1.5 mL) gave **20** (35 mg, 73%) as red needles: mp 160.5 °C; UV 247.5 (4.51), 296.5 (4.29), 315.5 (4.25), 476 (3.06) nm; IR 2216, 1708 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.93 (3 H, s, CO_2CH_3), 4.27 (3 H, s, OCH_3), 7.31 (1 H, d, J = 11.3 Hz, H-5), 7.47 (1 H, dd, J = 10.2, 9.9 Hz, H-7), 7.91 (1 H, ddd, J = 11.3, 9.9, 1.1 Hz, H-6), 8.28 (1 H, s, H-2), 9.68 (1 H, d, J = 10.2 Hz, H-8); ^{13}C NMR ($CDCl_3$) δ 50.4 (q, CO_2CH_3), 57.0 (q, OCH_3), 94.2 (s, *C*N), 113.9 (d, C-5), 117.3, 118.6 (s, C-1, C-3), 125.8 (d, C-7), 132.9, 139.4 (s, C-3a, C-8a), 140.2 (d, C-6), 140.6 (d, C-8), 141.3 (d, C-2), 164.7, 165.5 (s, C-4, CO_2CH_3). Anal. Calcd for $C_{14}H_{11}O_3N$: C, 69.70; H, 4.59; N, 5.80. Found: C, 69.21; H, 4.52; N, 5.44.

Ethyl 3-Cyano-4-methoxyazulene-1-carboxylate (21). Into a mixture of **19** (32 mg, 0.13 mmol) and ether (1 mL) was added CH_2N_2 (0.26 mmol/470 μL of ether). The mixture was stirred for 15 min at 0 °C and concentrated to give a red crude product, which was recrystallized from CCl_4 to give **21** (28.3 mg, 84%) as red crystals: mp 184 °C; UV 247.5 (4.65), 297 (4.42), 315.5 (4.33), 345.5 (3.96), 484.5 (3.15) nm; IR 2212, 1698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (3 H, t, J = 7.1 Hz, $CO_2CH_2CH_3$), 4.28 (3 H, s, OCH_3), 4.40 (2 H, q, J = 7.1 Hz, $CO_2CH_2CH_3$), 7.32 (1 H, d, J = 11.0 Hz, H-5), 7.48 (1 H, dd, J = 10.0, 9.9 Hz, H-7), 7.92 (1 H, dd, J = 11.0, 9.9 Hz, H-6), 8.32 (1 H, s, H-2), 9.71 (1 H, d, J = 10.9 Hz, H-8); ^{13}C NMR ($CDCl_3$) δ 14.5 (q, $CO_2CH_2CH_3$), 57.0 (q, OCH_3), 60.2 (t, $CO_2CH_2CH_3$), 94.2 (s, *C*N), 113.9 (d, C-5), 117.7, 118.6 (s, C-1, C-3), 125.8 (d, C-7), 132.9, 139.5 (s, C-3a, C-8a), 140.2 (d, C-6), 140.7 (d, C-8), 141.4 (d, C-2), 164.4, 165.5 (s, C-4, $CO_2CH_2CH_3$). Anal. Calcd for $C_{15}H_{13}O_3N$: C, 69.12; H, 5.39; N, 5.76. Found: C, 68.93; H, 5.04; N, 5.37.

Methyl 3-Cyano-4-acetoxyazulene-1-carboxylate (22). A mixture of **18** (68 mg, 0.3 mmol), acetic anhydride (2 mL), and pyridine (150 μL) was stirred for 2 h, poured into water (20 mL), and filtered to give a red crystalline crude product, which was recrystallized from CCl_4 to give **22** (59 mg, 73%) as red needles: mp 173 °C; UV 236 (4.48), 262.5 (3.99), 299.5 (4.45), 329 (3.90), 367.0 (3.80) nm; IR 2220, 1764, 1712 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.62 (3 H, s, $OCOCH_3$), 3.97 (3 H, s, CO_2CH_3), 7.56 (1 H, d, J = 11.1 Hz, H-5), 7.79 (1 H, ddd, J = 10.3, 9.8, 1.0 Hz, H-7), 8.02 (1 H, ddd, J = 11.1, 9.8, 1.1 Hz, H-6), 8.55 (1 H, s, H-2), 9.90 (1 H, dd, J = 10.3, 1.1 Hz, H-8); ^{13}C NMR ($CDCl_3$) δ 20.9 (q, $OCOCH_3$), 51.6 (q, CO_2CH_3), 94.2 (s, *C*N), 117.5, 118.2 (s, C-1, C-3), 126.5 (d, C-5), 129.8 (d, C-7), 136.6, 141.2 (s, C-3a, C-8a), 139.3 (d, C-6), 140.4 (d, C-8), 144.4 (d, C-2), 156.2 (s), 164.1 (s), 169.0 (s). Anal. Calcd for $C_{15}H_{11}O_4N$: C, 66.91; H, 4.12; N, 5.20. Found: C, 66.83; H, 3.83; N, 5.39.

Ethyl 3-Cyano-4-acetoxyazulene-1-carboxylate (23). Acetylation of **19** under the same reaction conditions mentioned above gave **23** in 53% yield as red needles: mp 133 °C; UV 236.5 (4.39), 263 (2.89), 299.5 (4.35), 330 (3.52), 367.5 (3.69) nm; IR 2220, 1768, 1708 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.44 (3 H, t, J = 7.1 Hz, $CO_2CH_2CH_3$), 2.62 (2 H, s, $OCOCH_3$), 4.43 (2 H, q, J = 7.1 Hz, $CO_2CH_2CH_3$), 7.54 (1 H, d, J = 11.0 Hz, H-5), 7.77 (1 H, ddd, J = 10.2, 10.0, 0.9 Hz, H-7), 8.00 (1 H, ddd, J = 11.0, 10.0, 0.8 Hz, H-6), 8.55 (1 H, s, H-2), 9.89 (1 H, d, J = 10.2 Hz, H-8); ^{13}C NMR ($CDCl_3$) δ 14.5 (q, $CO_2CH_2CH_3$), 21.0 (q, $OCOCH_3$), 60.6 (t, $CO_2CH_2CH_3$), 94.2 (s, *C*N), 117.6, 118.7 (s, C-1, C-3), 126.5 (d, C-5), 129.8 (d, C-7), 136.7, 141.4 (s, C-3a, C-8a), 139.3 (d, C-6), 140.5 (d, C-8), 144.5 (d, C-2), 156.3 (s), 163.8 (s), 169.1 (s). Anal. Calcd for $C_{16}H_{13}O_4N$: C, 67.84; H, 4.63; N, 4.95. Found: C, 67.37; H, 4.54; N, 4.82.

Diethyl 2-Diazo-2,6-azulenequinone-1,3-dicarboxylate (24).[1] Diazotization of diethyl 2-amino-6-bromoazulene-1,3-dicarboxylate with $NaNO_2$ and concd H_2SO_4 gave **24** (87% yield) as orange needles: mp 149 °C; UV 223.5 (4.23), 276 (4.25), 322.5 (4.66) nm; IR 2156, 1716 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 (6 H, t, J = 7.1 Hz, $CO_2CH_2CH_3$), 4.46 (4 H, q, J = 7.1 Hz, $CO_2CH_2CH_3$), 6.69 (2 H, d, J = 12.5 Hz, H-5, H-7), 8.37 (2 H, d, J = 12.5 Hz, H-4, H-8); ^{13}C NMR ($CDCl_3$) δ 14.1 (q, $CO_2CH_2CH_3$), 61.8 (t, $CO_2CH_2CH_3$), 85.8 (s, C-2), 120.9 (s, C-1, C-3), 132.2 (d, C-4, C-8), 133.1 (s, C-3a, C-8a), 133.4 (d, C-5, C-7), 161.6 (s, $CO_2CH_2CH_3$), 189.5 (s, C-6). Anal. Calcd for $C_{16}H_{14}O_5N_2$: C, 61.14; H, 4.49; N, 8.91. Found: C, 61.45; H, 4.27; N, 8.94.

1,3-Dicyano-2-diazo-2,6-azulenequinone (25).[1] Diazotization of 2-amino-6-bromo-1,3-dicyanoazulene with $NaNO_2$ and concd H_2SO_4 gave **25** (80% yield) as brown needles: mp 155 °C dec;[9] UV 218 (4.27), 235.5 (4.22), 261 (4.07), 321 (4.64), 366 (3.98) nm; IR 2224, 2156, 1620 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.66 (2 H, d, J = 12.1 Hz, H-5, H-7), 7.44 (2 H, d, J = 12.1 Hz, H-4, H-8); ^{13}C NMR (DMSO-d_6) δ 66.2 (s, C-2), 100.8 (s, *C*N), 111.6 (s), 129.9 (d, C-4, C-8), 133.1 (s), 134.0 (d, C-5, C-7), 187.3 (s, C-6). Anal. Calcd for $C_{12}H_4ON_4$: C, 65.44; H, 1.83; N, 25.44. Found: C, 65.17; H, 2.03; N, 25.63.

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(9) **Caution:** Diazo compound **25** occasionally explosively decomposes at 155 °C.