The Diazotization of 2-Aminoazulene Derivatives. The Formation of 2-Diazo-2,6-azulenoquinone Derivatives[1)]

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The Diazotization of 2-amino-6-bromo (or alkoxy)-azulene, with alkoxycarbonyl or cyano groups at the 1 and 3-positions, by sodium nitrite in dioxane–sulfuric acid afforded mainly the corresponding 2-diazo-2,6-azulenoquinone derivatives (**2a**, **2b**, **16**). The catalytic hydrogenation of these compounds gave 1,3-disubstituted 6-hydroxyazulenes (**4a**, **4b**, **18**), from which 1,3-disubstituted 6-alkoxy- or 6-acetoxy-azulenes were obtained. The diazotization of diethyl 2-amino-6-bromoazulene-1,3-dicarboxylate (**1a**) in dry benzene with isoamyl nitrite in the presence of hydrogen chloride afforded the 2,6-dichloroazulene derivative (**20**) and the 5-bromo-2-diazo-2,6-azulenoquinone derivative (**21**); the latter, accompanied by a bromine addition product (**22**), was also obtained by the bromination of **2a**. The diazotization of diethyl 2-aminoazulene-1,3-dicarboxylate (**25**) afforded **2a** and a deamination product (**26**). The structure and mechanism of the formation of these diazoazulenoquinones are discussed.

It has long been known that 1,3-disubstituted 2-aminoazulene derivatives easily undergo a diazo reaction similar to benzenoid amines, by way of which deamination products or 2-haloazulenes are obtained.[2)]

However, it has also been found that the deamination of diethyl 2-amino-6-bromoazulene-1,3-dicarboxylate does not proceed well under the same reaction conditions.[3)] We have studied the reaction for 2-aminoazulene derivatives and have found that the reaction afforded 2-diazo-2,6-azulenoquinone derivatives in good yields. The results will be reported in this paper.

Results and Discussion

When a solution of diethyl 2-amino-6-bromoazulene-1,3-dicarboxylate (**1a**)[4)] in dioxane containing concentrated sulfuric acid was diazotized with sodium nitrite, Compound **2a**, with a molecular formula of $C_{16}H_{14}O_5N_2$, was obtained, besides a small amount of diethyl 6-bromoazulene-1,3-dicarboxylate (**3**).[3)] We first assigned the structure of (A) (azulene diazocarboxylate derivative) to the compound **2a** formed by the intramolecular elimination of bromine by the ethoxyl group.[1)] However, from the facts that diethyl 6-acetoxy- and 6-chloroazulene-1,3-dicarboxylates were formed from **2a**, as will be described below, the structure of (A) was found to be incorrect.

Compound **2a** shows a UV absorption pattern similar to those of azulene derivatives, an IR (KBr) spectrum at 2165 cm^{-1} (diazonium group), and NMR ($CDCl_3$) signals at δ 6.61 ppm (2H) and 8.29 (2H), with an A_2B_2-type pattern. When Compound **2a** was submitted to catalytic hydrogenation in the presence of 5% Pd–C, no hydrogen absorption could be observed; however, the reaction yielded an acidic compound (**4a**), $C_{16}H_{16}O_5$, which gave methyl ether (**5a**), ethyl ether (**6**), and acetate (**7**) upon reaction with diazomethane, ethyl iodide with a silver salt of **4a**, and acetic anhydride respectively. Furthermore, Compound **4a** reacted with thionyl chloride to give a 6-chloro derivative (**8**), and it has already been reported that the hydrolysis, followed by the decarboxylation of **4a** with acid, afforded 6-hydroxyazulene.[5)]

Compound **6** was found to be identical with the known diethyl 6-ethoxyazulene-1,3-dicarboxylate obtained by the reaction of **3** with ethoxide;[3)] therefore, Compound **2a** must be diethyl 2-diazo-2,6-azulenoquinone-1,3-dicarboxylate or its inner salt. This compound is presumably formed by the nucleophilic attack of water on the 6-position of the initially-formed diazonium compound **9**, followed by the elimination of hydrogen bromide from an intermediate **10**. The attack at the 6-position must occur easily, because the position is activated by an electron-attractive diazonium group at the 2-position and by ethoxycarbonyl groups at the 1- and 3-positions, especially under acidic conditions.

The fact that the apparent hydrogen absorption could not be observed in the catalytic hydrogenation of **2a** can be explained by the liberation of an equimolar amount of nitrogen probably through an intermediate **11** when hydrogen is absorbed.

The nucleophilic substitution of Compound **1a** afforded the corresponding azulenes, the 6-ethoxy (**12**), 6-ethylthio (**13**), and 6-*p*-tolylthio (**14**) derivatives. However, the reaction of **1a** with methoxide in methanol afforded dimethyl 2-amino-6-bromoazulene-1,3-dicarboxylate (**1b**) as insoluble precipitates.

The similar diazotization of **12** and **13** yielded the same compound **2a** in good yields. The diazotization of **1b** afforded dimethyl ester (**2b**) in a good yield. The catalytic reduction of **2b** gave the 6-hydroxyazulene derivative (**4b**), the reaction of which with diazomethane afforded the corresponding methyl ether (**5b**). The heating of these diazoazulenoquinones (**2a** and **2b**) in isopropyl alcohol in the presence of HCl or H_2SO_4 for a short time yielded the corresponding 6-hydroxyazulene derivatives (**4a** and **4b** respectively) and acetone by disproportionation, followed by the extrusion of N_2.

The diazotization of the 2-amino-6-bromo-1,3-

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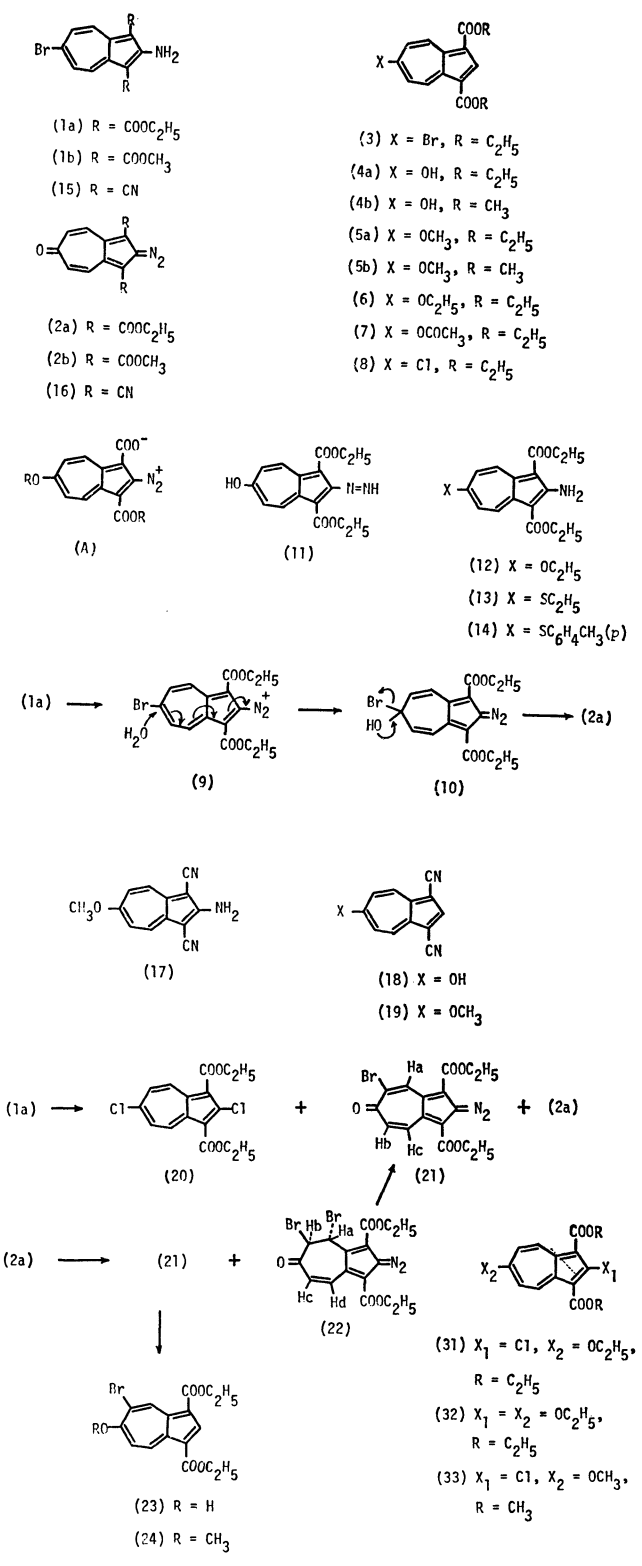
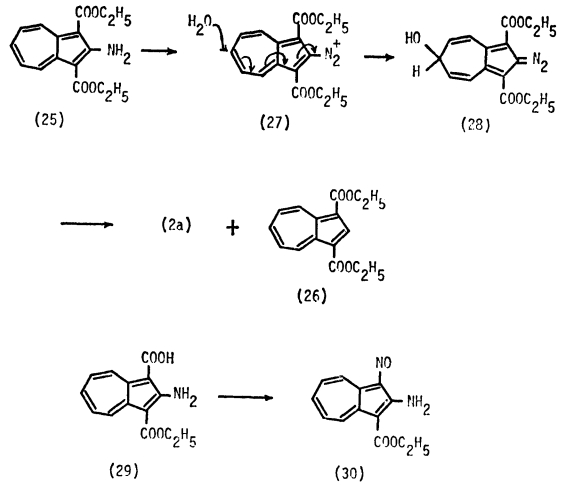


dicyanoazulene (**15**) obtained by the bromination of 2-amino-1,3-dicyanoazulene[2] in acetic acid at an elevated temperature afforded a similar diazo compound, 1,3-dicyano-2-diazo-2,6-azulenoquinone (**16**), which was also obtained by the diazotization of 2-amino-6-methoxy-1,3-dicyanoazulene (**17**). The structure of **16** was confirmed by reduction to yield unstable 6-hydroxy-1,3-dicyanoazulene (**18**), followed by methylation which gave 6-methoxy-1,3-dicyanoazulene (**19**), and by the IR spectrum of **16**, which shows a diazonium band at 2155 cm^{-1} and a cyano band at 2217 cm^{-1}.



On the other hand, when a solution of **1a** in dry benzene containing dry hydrogen chloride was diazotized with isoamyl nitrite, diethyl 2,6-dichloroazulene-1,3-dicarboxylate (**20**), a compound **21** with the molecular formula of $C_{16}H_{13}O_5N_2Br$, and a small amount of **2a** were obtained. Compound **21** shows an UV absorption curve similar to that of **2a**; IR (KBr) 2175 cm^{-1}; NMR ($CDCl_3$) δ 6.71 ppm (d, J=12.5 Hz, Hb), 8.01 (d, J=12.5 Hz, Hc), and 9.08 (s, Ha). From the above data, as well as on the basis of following reactions, Compound **21** was assumed to be diethyl 5-bromo-2-diazo-2,6-azulenoquinone-1,3-dicarboxylate, which must be formed by the bromination of the initially-formed diazoazulenoquinone (**2a**); the bromine might have been produced by the oxidation of liberated hydrogen bromide under these conditions. Therefore, it is reasonable that a similar diazotization of the 6-ethoxyazulene derivative (**12**) in benzene–HCl with isoamyl nitrite afforded only Compound **2a**.

The bromination of **2a** with bromine in $CHCl_3$ actually afforded Compound **21**, accompanied by a bromine addition product (**22**), and the treatment of **22** with triethylamine afforded **21** in a quantitative yield. The dibromide (**22**) was assumed to have the structure shown in the scheme on the basis of its derivation to **21**, the results of elemental analysis, and NMR spectrum ($CDCl_3$) δ 4.82 ppm (d, d, J=6.0, 1.8 Hz, Hb), 6.12 (d, d, J=13.0, 1.8 Hz, Hc), 6.56 (d, J=6.0 Hz, Ha), and 8.06 (d, J=13.0 Hz, Hd).

Compound **21** was catalytically hydrogenated to yield the 5-bromo-6-hydroxyazulene derivative (**23**), which was then reacted with diazomethane to give the methyl ether (**24**).

The formation of the dichloro compound (**20**) can be explained by a nucleophilic replacement of the bromine of the diazonium compound (**9**) by the chloride ion, followed by a Sandmeyer reaction at the 2-position. No change was observed in the reaction of **1a** and hydrogen chloride; therefore, it is clear that halogen exchange occurred after diazotization.

When diethyl 2-aminoazulene-1,3-dicarboxylate

(**25**)[2] was diazotized in dioxane containing sulfuric acid with sodium nitrite, diazoazulenoquinone (**2a**) and a deamination product, diethyl azulene-1,3-dicarboxylate (**26**), were unexpectedly obtained, although in low yields. This reaction may be explained as follows; at first the diazotization of **25** occurs to yield diazonium compound (**27**), which is easily attacked by water at the 6-position to give the quinol compound (**28**); then dispropotionation occurs between **27** and **28** to afford **26** and **2a** respectively.

The fact that the diazonium compound (**27**) undergoes a nucleophilic attack at the 6-position, in contrast with the reactivity of azulene itself, which preferentially occurs at the 4-position,[6] may be attributable to the steric hindrace of ethoxycarbonyl groups at the 1 and 3 positions.

The diazotization of 2-amino-3-ethoxycarbonylazulene-1-carboxylic acid (**29**) was attempted in the anticipation of obtaining a diazoazulenecarboxylate derivative; however, only a violet powder was obtained, and upon treatment with sodium carbonate it yielded ethyl 2-amino-3-nitrosoazulene-1-carboxylate (**30**), which had been synthesized by the nitrosation of ethyl 2-aminoazulene-1-carboxylate.[7]

When the dichloroazulene derivative (**20**) was treated with ethoxide in ethanol, 2-chloro-6-ethoxyazulene and 2,6-diethoxyazulene derivatives (**31** and **32**) were obtained, depending on the amount of the reagent used. The alkaline hydrolysis of **20** afforded 2-chloro-6-hydroxyazulene-1,3-dicarboxylic acid as an amorphous powder, which then gave dimethyl 2-chloro-6-methoxyazulene-1,3-dicarboxylate (**33**) upon reaction with diazomethane.

The 2-diazo-2,6-azulenoquinone derivatives obtained in this paper are very stable, with definite melting points; they are soluble in non-polar solvents such as $CHCl_3$ and benzene, less soluble in alcohol, and insoluble in water.

The electronic spectra of the diazoazulenoquinones in MeOH, acidic, and basic media (Fig. 1 and see Experimental section) show that the spectra are little changed by the solvent used and do not show any absorption maxima over 450 nm.

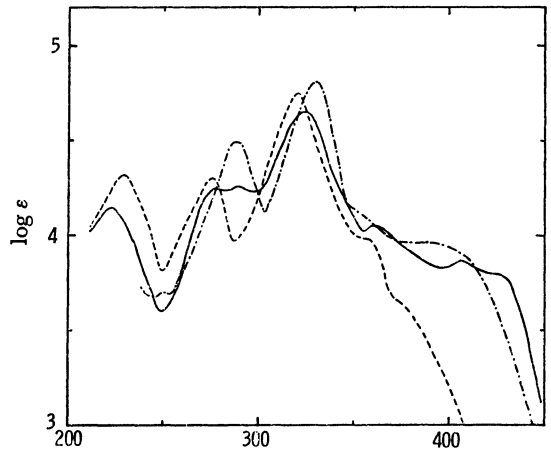
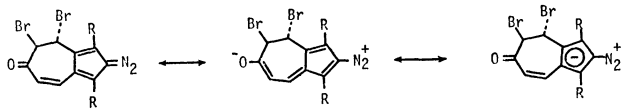


Fig. 1. UV absorption spectra of compound (**2a**) in MeOH (——), in MeOH-HCl (----) and in MeOH-NaOH (—·—·—).

The infrared spectra of the compounds show strong diazonium bands at 2155—2175 cm^{-1}, a frequency a little higher than those of *p*-diazobenzoquinone, 2100 cm^{-1},[8] and diazocyclopentadiene, 2082 cm^{-1},[9] but considerably lower than that of benzene diazonium tetrafluoroborate, 2298 cm^{-1}.[8]

These facts would indicate that the compounds exist in the following resonance hybrids:

The ultraviolet absorption spectrum of the rather stable dibromo compound (**22**) is completely different from those of azulene compounds, and the infrared spectrum shows a diazonium band at 2135 cm^{-1} and a broad carbonyl band at 1690—1655 cm^{-1}. The compound seems to be stabilized by the contribution of the following resonance forms, as is also observed in diazocyclopentadiene.[9]



Experimental[10]

*The Diazotization of Diethyl 2-Amino-6-bromoazulene-1,3-dicarboxylate (**1a**) and Related Compounds (**1b**, **12**, **13**, **15**, and **17**).* *a) In Dioxane*: To a stirred solution of **1a** (300 mg) in purified dioxane (7 ml) and concentrated sulfuric acid (1 ml), a solution of sodium nitrite (150 mg) in water (1 ml) was added over a 3-hr period under cooling with ice. After the mixture had been stirred for 2 hr, water (20 ml) was added and the separated precipitates were collected, washed, and recrystallized from benzene to give 190 mg of diethyl 2-diazo-2,6-azulenoquinone-1,3-dicarboxylate (**2a**). The filtrate of the recrystallization was chromatographed on an alumina column and eluted with benzene. From the first effluent 10 mg of 6-bromoazulene-1,3-dicarboxylate (**3**) was obtained; it was identified by a direct comparison of the infrared spectrum with that of an authentic specimen.[3]

In a similar manner, five compounds (**1a**, **12**, **13**, **15**, and **17**) gave the corresponding 2-diazo-2,6-azulenoquinones (**2b**, **2a**, and **16**). The analytical and physical data of the products are as follows.

2a: orange needles, mp 148—149 °C (decomp.).

Found: C, 61.45; H, 4.27; N, 8.94%. Calcd for $C_{16}H_{14}O_5N_2$: C, 61.14; H, 4.49; N, 8.91%.

λ_{max}^{MeOH} nm (log ε); 223 (4.15), 277 (4.25), 289 (4.26), 324 (4.65), 360 (4.05), 406 (3.87) and 426^{sh} (3.80).

$\lambda_{max}^{MeOH-HCl}$ nm (log ε); 229 (4.32), 276 (4.30), 321 (4.75), 358^{sh} (3.98) and 373^{sh} (3.66).

$\lambda_{max}^{MeOH-NaOH}$ nm (log ε); 250 (3.84), 288 (4.39), 330 (4.81), 358^{sh} (4.14) and 390 (3.97).

2b: orange needles (from benzene), mp 173—175 °C.

Found: C, 58.66; H, 3.70; N, 9.86%. Calcd for $C_{14}H_{10}O_5N_2$: C, 58.74; H, 3.52; N, 9.79%.

λ_{max}^{MeOH} nm (log ε); 223 (4.11), 278 (4.20), 289 (4.20), 325 (4.69), 360 (3.98), 406 (3.90) and 426 (3.85).

$\lambda_{max}^{MeOH-HCl}$ nm (log ε); 228 (4.32), 275 (4.29), 320 (4.76),

359 (3.98), and 374 (3.63).
$\lambda_{max}^{MeOH-NaOH}$ nm (log ε); 250 (3.60); 287 (4.37), 329 (4.81), 360^{sh} (4.11), and 390 (3.92).

16: brown prisms (from dioxane), mp 155 °C (explosively decomp.).

Found: C, 65.17; H, 2.03; N, 25.63%. Calcd for $C_{12}H_4ON_4$: C, 65.44; H, 1.83; N, 25.44%.
λ_{max}^{MeOH} nm (log ε); 235 (3.97), 262^{sh} (3.94), 274^{sh} (4.01), 315^{sh} (4.27), 323 (4.29), 375^{sh} (3.86), and 400 (3.93).
$\lambda_{max}^{MeOH-HCl}$ nm (log ε); 225 (4.21), 265 (3.88), 315^{sh} (4.39), 319 (4.40), 374 (3.82), 396 (3.79), and 420 (3.70).
$\lambda_{max}^{MeOH-NaOH}$ nm (log ε); 246 (4.07), 262 (3.96), 271 (3.92), 324 (4.50), and 399 (3.86).

b) In dry benzene: A solution of **1a** (2 g) in dry benzene (100 ml) was saturated with dry hydrogen chloride gas under cooling with ice, and then isoamyl nitrite (1.5 ml) was added to the solution. After the mixture had been allowed to stand in an ice box overnight, benzene (100 ml) was added and the solution was washed with water five times. After the benzene solution had then been dried over anhydrous sodium sulfate, the solution was concentrated to about 30 ml under reduced pressure. The solution was submitted to column chromatography on an alumina and then eluted with benzene. From the first effluent, 300 mg of diethyl 2,6-dichloroazulene-1,3-dicarboxylate (**20**) as reddish-purple crystals (mp 160—161 °C (from benzene–cyclohexane)) were obtained.

Found: C, 56.02; H, 3.95%. Calcd for $C_{16}H_{14}O_4Cl_2$: C, 56.30; H, 4.13%.
λ_{max}^{MeOH} nm (log ε); 237 (4.31), 266 (4.05), 305 (4.54), 315 (4.60), 349^{sh} (3.68), 362 (3.77), and 500 (2.54).

The latter effluents were combined and rechromatographed on an alumina column; 1.1 g of diethyl 5-bromo-2-diazo-2,6-azulenoquinone-1,3-dicarboxylate (**21**) as orange needles (mp 166—168 °C (decomp.) (from benzene)) were thus obtained.

Found: C, 49.05; H, 3.28; N, 7.26%. Calcd for $C_{16}H_{13}O_5N_2Br$: C, 48.87; H, 3.33; N, 7.13%.
λ_{max}^{MeOH} nm (log ε); 229 (4.11), 280 (4.20), 292 (4.25), 323^{sh} (4.55), 334 (4.62), 264^{sh} (4.01), 382^{sh} (3.83) and 410^{sh} (3.42).
$\lambda_{max}^{MeOH-HCl}$ nm (log ε); 232 (4.19), 277 (4.19), 322 (4.64), 356^{sh} (3.95), 383 (3.81) and 430^{sh} (3.22).
$\lambda_{max}^{MeOH-NaOH}$ nm (log ε); 245 (4.01); 289 (4.35), 333 (4.73), 360^{sh} (4.12), and 398^{sh} (3.88).

From the latter effluent, 80 mg of Compound **2a** (mp 148 °C (decomp.)) were obtained.

A similar diazotization of Compound **12** in dry benzene afforded only **2a**.

*The Diazotization of Diethyl 2-Aminoazulene-1,3-dicarboxylate (**25**) in Dioxane.* To a solution of Compound **25** (500 mg) in dioxane (5 ml) and concentrated sulfuric acid (1.5 ml), a solution of sodium nitrite (250 mg) in water (1 ml) was added under cooling with ice. The solution was then stirred overnight, water (30 ml) was added, and the solution was extracted with benzene. The extract was washed with water, dried, and submitted to chromatography on an alumina column. From the first effluent 50 mg of reddish crystals (mp 120 °C) were obtained; their infrared spectrum was superimposable upon that of authentic diethyl azulene-1,3-dicarboxylate (**26**).[2b] From the next effluent, 70 mg of Compound **2a** were obtained. From the latter effluents, a dark brown oil was obtained; however, its structure could not be clarified.

*The Reaction of 2-Amino-3-ethoxycarbonylazulene-1-carboxylic Acid (**29**) with Nitrous Acid.* To a stirred solution of **29** (140 mg) in dioxane (5 ml) and concentrated sulfuric acid (0.5 ml), isoamyl nitrite (0.1 g) was added under cooling with ice. After the mixture had been stirred for 30 min, the resulting precipitate was filtered to give black violet crystals (mp 199—201 °C (decomp.)). The crystals were dissolved in water, and the solution was neutralized by sodium hydrogen carbonate to afford ethyl 2-amino-1-nitrosoazulene-3-carboxylate (**30**) in a quatitative yield. The infrared spectrum of Compound **30** was superimposable upon that of an authentic sample.[7]

The Hydrogenation of 2-Diazo-2,6-azulenoquinones to 6-Hydroxyazulenes. A solution of **2a** (300 mg) in ethanol (100 ml) was submitted to catalytic hydrogenation in the presence of 5% Pd–C (30 mg), after which the solution was shaken for 3 hr. Hydrogen was not takenup, to all appearances. The catalyst was then filtered off, the solvent was removed, and the residue was recrystallized from benzene to give 200 mg of diethyl 6-hydroxyazulene-1,3-dicarboxylate (**4a**) as yellow needles (mp 171—172 °C).

Found: C, 66.79; H, 5.46%. Calcd for $C_{16}H_{16}O_5$: C, 66.65; H, 5.59%.
λ_{max}^{MeOH} nm (log ε); 225 (4.33), 278 (4.42), 323 (4.75), 330^{sh} (4.67), 356^{sh} (4.12), 374 (3.90), 395^{sh} (3.56) and 464 (2.74).

A similar hydrogenation of **2b** and **21** afforded the corresponding 6-hydroxyazulenes (**4b** and **23**).

4b: yellow needles, mp 235—237 °C (decomp.).

Found: C, 64.73; H, 4.40%. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65%.

23: dark yellow needles, mp 203—205 °C (decomp.).

Found: C, 52.51; H, 4.03%. Calcd for $C_{16}H_{15}O_5Br$: C, 52.30; H, 4.12%.
λ_{max}^{MeOH} nm (log ε); 235 (4.28), 280 (4.35), 293 (4.26), 326 (4.71), 383 (4.01), 410^{sh} (3.55) and 475^{sh} (2.95).

6-Methoxyazulenes from 6-Hydroxyazulenes. Thirty mg of Compound **4a** was methylated with diazomethane in methanol. The crystals obtained by the removal of the solvent were dissolved in benzene, and the solution was passed through an alumina column and then recrystallized from a mixture of benzene and cyclohexane to give 25 mg of **5a** as reddish prisms (mp 140—141 °C).

In a similar manner, two compounds (**4b** and **23**) gave the corresponding 6-methoxyazulenes (**5b** and **24**); the hydrogenation of **16**, followed by its methylation afforded 1,3-dicyano-6-methoxyazulene (**19**). The analytical and physical data of the products are as follows.

5a: Found: C, 67.60; H, 5.78%. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00%.
λ_{max}^{MeOH} nm (log ε); 228 (4.46), 276 (4.40), 310^{sh} (4.65), 321 (4.77), 349 (4.06), 376 (3.75), and 456 (3.00).

5b: orange needles, mp 144—146 °C.

Found: C, 65.92; H, 5.31%. Calcd for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15%.
λ_{max}^{MeOH} nm (log ε); 233 (4.40), 276 (4.36), 307^{sh} (4.60), 320 (4.76), 348 (4.03), 374 (3.81), and 453 (3.04).

24: reddish crystals, mp 133—134 °C.

Found: C, 53.71; H, 4.30%. Calcd for $C_{17}H_{17}O_5Br$: C, 53.56; H, 4.49%.
λ_{max}^{MeOH} nm (log ε); 237 (4.32), 270^{sh} (4.27), 279 (4.34), 312^{sh} (4.65), 325 (4.84), 355 (4.04), 386 (4.08), and 470 (3.03).

19: orange needles, mp 245 °C (decomp.).

Found: C, 74.76; H, 4.17; N, 13.17%. Calcd for $C_{13}H_8ON_2$: C, 74.99; H, 3.87; N, 13.46%.
λ_{max}^{MeOH} nm (log ε); 220 (4.38), 227 (4.38), 265 (3.94), 306^{sh} (4.55), 313^{sh} (4.68), 318 (4.71), 352 (3.96), and 460 (2.98).

6-Methoxyazulenes from 6-Haloazulenes. *a)*: A solution of 2-amino-6-bromo-1,3-dicyanoazulene (**15**) (816 mg) in methanol (40 ml) containing 200 mg of sodium was refluxed for 5 hr. After cooling, greenish-yellow needles (640 mg) were obtained. Recrystallization from dioxane gave 2-amino-6-methoxy-1,3-dicyanoazulene (**17**) as yellow needles (mp 285 °C (decomp.)).

Found: C, 69.52; H, 4.04; N, 18.67%. Calcd for $C_{13}H_9ON_3$: C, 69.94; H, 4.06; N, 18.83%.

b): A solution of **20** (100 mg) in 50% ethanol (10 ml) containing potassium hydroxide (1 g) was refluxed for 2 hr. Water (20 ml) was then added, and the solution was acidified by the addition of 2M hydrochloric acid. A dark yellow solid was filtered off, washed with water, and dried. A suspended solution of the solid in methanol was methylated with diazomethane, the solvent was removed, and the residue was recrystallized from ethanol to give dimethyl 2-chloro-6-methoxyazulene-1,3-dicarboxylate (**33**) (30 mg) as orange needles (mp 140—142 °C).

Found: C, 58.58; H, 4.15%. Calcd for $C_{15}H_{13}O_5Cl$: C, 58.33; H, 4.23%.

λ_{max}^{MeOH} nm (log ε); 228 (4.38), 275 (4.32), 310^{sh} (4.71), 320 (4.82), 364 (4.11), and 440 (3.16).

6-Ethoxyazulenes. *a)*: A dried silver salt obtained from 130 mg of **4a** was suspended in dry benzene (20 ml), and the solution was refluxed with ethyl iodide (500 mg) for 3 hr. The black precipitate was then filtered off, and the solvent was removed from the filtrate to leave orange crystals. Recrystallization from a mixture of benzene and methanol gave 45 mg of diethyl 6-ethoxyazulene-1,3-dicarboxylate (**6**) as orange needles (mp 139—141 °C).

Found: C, 68.31; H, 6.36%. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37%.

λ_{max}^{MeOH} nm (log ε); 228 (4.41), 276 (4.37), 308^{sh} (4.62), 320 (4.78), 349 (4.07), 375 (3.85), and 454 (3.04).

b): After a solution of Compound **1a** (300 mg) in anhydrous ethanol (20 ml) containing 200 mg of sodium had been refluxed for 2 hr, orange crystals which were precipitated out by cooling the reaction mixture were recrystallized from benzene to afford diethyl 2-amino-6-ethoxyazulene-1,3-dicarboxylate (**12**) (160 mg) as yellow needles (mp 160—161 °C).

Found: C, 65.52; H, 6.11%. Calcd for $C_{18}H_{21}O_5N$: C, 65.24; H, 6.39%.

λ_{max}^{MeOH} nm (log ε); 232^{sh} (4.28), 245^{sh} (4.37), 255 (4.39), 281 (4.27), 325^{sh} (4.66), 336 (4.77), 370^{sh} (3.90), 410 (3.89) and 460 (3.86).

c): A solution of Compound **20** (100 mg) in anhydrous ethanol (10 ml) containing sodium ethoxide prepared from 7 mg of sodium was refluxed for one hour. A usual working up afforded 65 mg of diethyl 2-chloro-6-ethoxyazulene-1,3-dicarboxylate (**31**) as orange needles (from benzene) (mp 137—138 °C).

Found: C, 61.52; H, 5.30%. Calcd for $C_{18}H_{19}O_5Cl$: C, 61.63; H, 5.46%.

λ_{max}^{MeOH} nm (log ε); 229 (4.38), 276 (4.30), 311^{sh} (4.71), 321 (4.82), 365 (4.02), and 445 (3.10).

d): A solution of Compound **20** (100 mg) in anhydrous ethanol (10 ml) containing sodium ethoxide prepared from 60 mg of sodium was refluxed for 2 hr. A usual working up gave diethyl 2,6-diethoxyazulene-1,3-dicarboxylate (**32**) as orange needles (from benzene) (mp 148—149 °C).

Found: C, 66.85; H, 6.82%. Calcd for $C_{20}H_{24}O_6$: C, 66.65; H, 6.71%.

λ_{max}^{MeOH} nm (log ε); 229 (4.44), 273 (4.34), 313^{sh} (4.71), 323 (4.82), 365 (4.07), and 436 (3.10).

*Diethyl 2-Amino-6-ethylthioazulene-1,3-dicarboxylate (**13**).* A solution of **1a** (200 mg) and ethylmercaptane (45 mg) in anhydrous ethanol (5 ml) containing 14.5 mg of sodium was refluxed for one hour. The orange crystals which precipitated out were filtered, washed with water, and recrystallized from ethanol to give 170 mg of **13** as orange crystals (mp 104—105 °C).

Found: C, 62.42; H, 5.87; N, 3.95%. Calcd for $C_{18}H_{21}O_4NS$: C, 62.24; H, 6.10; N, 4.03%.

λ_{max}^{MeOH} nm (log ε); 246 (4.50), 277 (4.17), 345 (4.73), 432 (4.18), and 485 (3.66).

*Diethyl 2-Amino-6-(p-tolylthio)azulene-1,3-dicarboxylate (**14**).* The reaction of **1a** (200 mg) and *p*-thiocresol in anhydrous ethanol in the presence of sodium ethoxide afforded 190 mg of **14** as orange needles (from ethanol) (mp 129—130 °C).

Found: C, 67.57; H, 5.49; N, 3.32%. Calcd for $C_{23}H_{29}O_4NS$: C, 67.46; H, 5.66; N, 3.42%.

λ_{max}^{MeOH} nm (log ε); 246 (4.54), 277 (4.23), 344 (4.73), 433 (4.22), and 480 (3.70).

*Dimethyl 2-Amino-6-bromoazulene-1,3-dicarboxylate (**1b**).* The refluxing of a solution of Compound **1a** (300 mg) in anhydrous methanol containing 200 mg of sodium afforded orange crystals, which were subsequently purified by chromatography and recrystallization from chloroform to give **1b** (220 mg) as orange needles (mp 203—204 °C).

Found: C, 50.05; H, 3.40; N, 4.12%. Calcd for $C_{14}H_{12}O_4NBr$: C, 49.72; H, 3.57; N, 4.14%.

λ_{max}^{MeOH} nm (log ε); 244 (4.57), 276 (4.18), 320 (4.69), 333 (3.90), 404^{sh} (3.96), 416 (3.97), and 473 (3.58).

*2-Amino-6-bromo-1,3-dicyanoazulene (**15**).* A mixture of 2-amino-1,3-dicyanoazulene (1.76 g), bromine (3.5 g), and sodium acetate (1.23 g) in acetic acid (50 ml) was heated at 60 °C for 7 hr. The crystals (2.3 g) which separated out were filtered and recrystallized from dioxane to give 2-amino-6-bromo-1,3-dicyanoazulene (**15**) (2.3 g) as yellowish-brown needles (mp over 300 °C).

Found: C, 52.84; H, 2.45; N, 15.14%. Calcd for $C_{12}H_6N_3Br$: C, 52.99; H, 2.24; N, 15.45%.

λ_{max}^{MeOH} nm (log ε); 231 (4.59), 252^{sh} (4.08), 270 (3.83), 315 (4.79), 328 (4.86), 416^{sh} (4.00), and 418 (4.01).

*The Bromination of Diethyl 2-Diazo-2,6-azulenoquinone-1,3-dicarboxylate (**2a**).* To a stirred solution of Compound **2a** (200 mg) in chloroform (5 ml), a solution of bromine (105 mg) in chloroform (1 ml) was added at room temperature over a 30-min period. After having been stirred a further hour, the solution was washed with water, dried, and chromatographed on a silica gel column. The first effluent, obtained by the use of $CHCl_3$–CCl_4 (2 : 1), gave 100 mg of a dark yellow viscous oil, and the second effluent, obtained by the use of $CHCl_3$, gave 80 mg of diethyl 5-bromo-2-diazo-2,6-azulenoquinone-1,3-dicarboxylate (**21**); these substances were identified by a comparison of their infrared spectra. From the last effluent, the starting azulene (**2a**) (30 mg) was recovered. The dark yellow viscous oil obtained from the first effluent could not be crystallized; it was found to be the bromine addition compound **22** from the spectroscopic data.

Found: N, 5.64%. Calcd for $C_{16}H_{14}O_5N_2Br_2$: N, 5.91%.

λ_{max}^{MeOH} nm (log ε); 217 (4.33), 295 (4.16), 335 (4.20), and 385 (4.17). A solution of Compound **22** (70 mg) in chloroform (3 ml) was treated with 5 drops of triethylamine; the solution was thus immediately changed to dark yellow, and from it 40 mg of Compound **21** were obtained.

*Diethyl 6-Acetoxyazulene-1,3-dicarboxylate (**7**).* The acetate **7** was obtained as reddish-purple needles by the reaction of Compound **4a** with acetic anhydride in the presence of pyridine (mp 133—134 °C).

Found: C, 65.22; H, 5.60%. Calcd for $C_{18}H_{18}O_6$: C, 65.44; H, 5.49%.

λ_{max}^{MeOH} nm (log ε); 233 (4.45), 271 (4.36), 296^{sh} (4.54), 307 (4.65), 331 (4.05), 362 (3.90), 373 (3.97), and 497 (3.80).

*Diethyl 6-Chloroazulene-1,3-dicarboxylate (**8**).* A solution of Compound **4a** (480 mg) and thionyl chloride (3 ml) in anhydrous benzene (50 ml) was allowed to stand overnight and was then gently refluxed for 30 min. After the solvent

had been removed, a solution of the residue in benzene was chromatographed on an alumina column to give Compound **8** (290 mg) as reddish-purple needles (mp 200—201 °C).

Found: C, 62.76; H, 5.05%. Calcd for $C_{16}H_{15}O_4Cl$: C, 62.65; H, 4.93%.

λ_{max}^{MeOH} nm (log ε); 236 (4.54), 270 (4.29), 300 (4.69), 311 (4.81), 337^{sh} (3.88), 345 (3.93), 375 (4.00) and 510 (3.08).

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