Nonbenzenoid Aromatic Systems. XII.[1a] Synthesis of 2-, 3-, and 6-Substituted 2-(1-Azulyl)ethanols and Their Tosylate Esters

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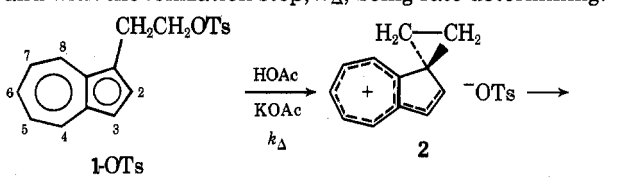
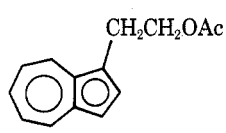
The synthesis of 2- (CH_3O, CH_3, Cl, Br, I, CN) and 3-substituted (CH_3O, CH_3, CH_3S, Br, $COCH_3$, CN, NO_2) derivatives of 2-(1-azulyl)ethanol (1-OH) and 1-OAc by combining conventional procedures are reported. A method for the protodeamination of diethyl 2-amino-6-bromoazulene-1,3-dicarboxylate (3) to diethyl 6-bromoazulene-1,3-dicarboxylate (7) in 93% yield using *p*-hydroquinone as in situ reducing agent of the intermediate diazonium salt is described. 7 and diethyl 6-methoxyazulene-1,3-dicarboxylate were found to hydrolyze when dissolved in concentrated sulfuric acid and then the yellow solution poured into water in excellent yields. The resulting 1,3-diacids were then thermally decarboxylated to 6-bromo- (16) and 6-methoxyazulene (17), respectively. Direct β-hydroxyethylation (ethylene oxide and $AlCl_3$) of 16, 17, and 6-methylazulene gave the respective 6-X-1-OH's. 6-CN-1-OH was prepared from the reaction of 6-Br-1-OAc and cuprous cyanide in DMF followed by hydrolysis. The tosylate esters of these derivatives of 1-OH were generally prepared in ether with powdered potassium hydroxide and *p*-toluenesulfonyl chloride. The substituent effects on λ_{max} of azulene in the visible spectra of the above derivatives are discussed.

In 1971 we reported certain preliminary results on the buffered acetolysis of 2-(1-azulyl)ethyl tosylate (1-OTs) demonstrating that the 1-azulyl substituent was a "superparticipator" in β-arylethyl arenesulfonate solvolyses[2] with $k_{1\text{-OTs}}/k_{PhCH_2CH_2OTs} \sim 10^5$ for the k_Δ process at 25 °C.[3] Buffered acetolysis of 1-OTs was shown to proceed exclusively by the k_Δ process in the absence of ion-pair return and with the ionization step, k_Δ, being rate determining.[3]



1-OTs 2



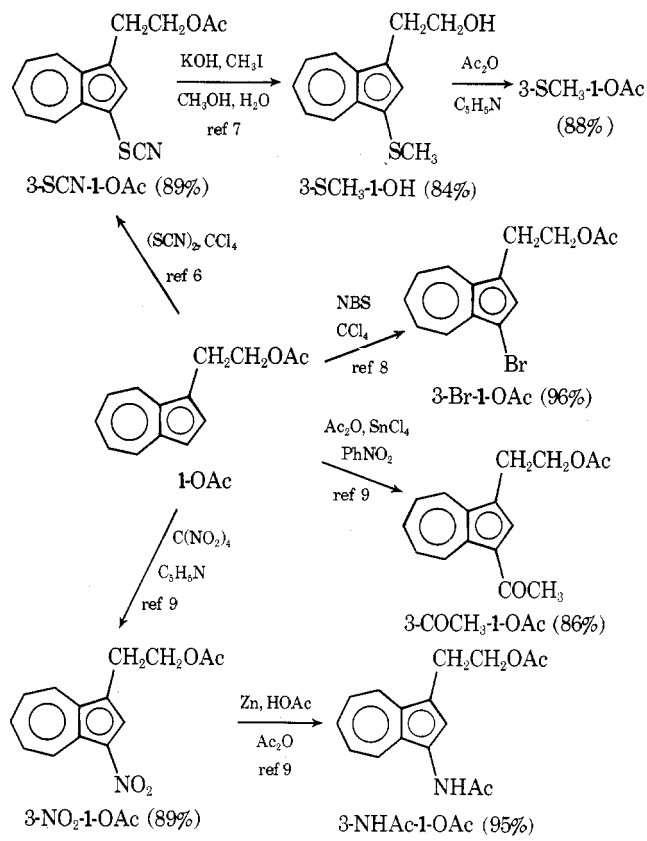
1-OAc

With these primary points established, it became of interest to us to consider how substituents at the seven nonequivalent ring positions in 1-OTs and 2 would influence this k_Δ process. Before such studies could be carried out, appropriate synthetic procedures leading to the desired derivatives must, of course, be developed. It is the syntheses of derivatives of 1-OH at the three most diverse positions, the 2 (benzene ortholike), the 3 (benzene metalike), and the 6 position (long-range benzene paralike), that we wish to describe here.

Two methods are available for introducing the β-ethanol side chain onto the azulene 1 position. The first is the method of Anderson,[4] which involves electrophilic N,N-dimethylaminomethylation, quaternerization with CH_3I, displacement with CN (→ $-CH_2CN$), hydrolysis (→ $-CH_2CO_2H$), and diborane reduction to 1-OH. This was the procedure used in our initial studies, and is most convenient for specific C_α–D_2 labeling with B_2D_6 reduction of 1-azulylacetic acid. The second method involves direct β-hydroxyethylation of azulenes with ethylene oxide and $AlCl_3$[5] and was the method of choice in our later syntheses.

Synthesis of 3-Substituted 1-OH's. The pioneering research of Anderson and his co-workers at the University of Washington in the 1950's and 1960's established the ease and generality of electrophilic substitution at the 1(3) position of azulene and various substituted derivatives. With

Scheme I



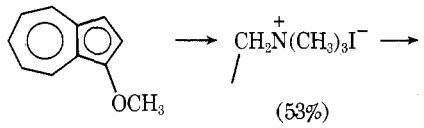
quantities of 1-OH and 1-OAc available by either of the above procedures, the range of desired 3-X-1-OH's (or acetates) was prepared by established methods outlined in Scheme I. Use of the mild nitrating reagent tetranitromethane in pyridine[9] also allowed for direct nitration of 1-OH to 3-NO_2-1-OH in 92% yield.

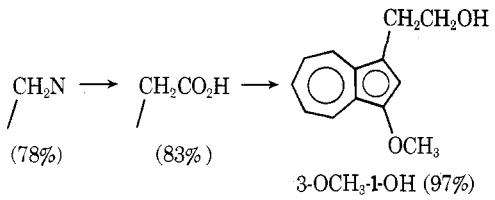
3-CN-1-OAc was prepared in 32% yield by allowing 3-Br-1-OAc to react with cuprous cyanide in refluxing dimethylformamide (DMF). Direct cyanation of 1-OAc with cyanogen bromide and stannic chloride[10] gave 3-CN-1-OAc in 19% yield.

3-CH_3-1-OH was prepared by N,N-dimethylaminomethylation[4] of 1-OH followed by quaternization of the tertiary

amine with methyl iodide; the yield of the iodide salt was 87%. Reduction of this quaternary salt with sodium borohydride in ethanol under reflux for 7 min gave a 51% yield of 3-CH_3-1-OH which was unstable in the presence of traces of acids. Direct β-hydroxyethylation[5] of 1-methylazulene produced only decomposition.

The synthesis of 3-OCH_3-1-OH starts with 1-methoxyazulene[11] and uses Anderson's stepwise construction of the β-ethanol side chain[4] as shown below. Here also, direct β-hydroxyethylation[5] gave only decomposition.

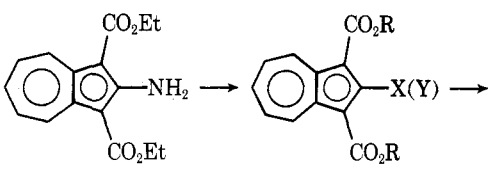




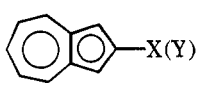
3-OCH_3-1-OH (97%)

The 3-X-1-OH or 3-X-1-OAc derivatives thus available are X = CH_3O, CH_3, H, SCH_3, Br, $COCH_3$, CN, and NO_2.

Synthesis of 2-Substituted 1-OH's. The preparation of 2-substituted 1-OH's (also 6-X-1-OH's) utilized the elegant Nozoe azulene synthesis where a substantial number of 2-substituted azulenes have been reported.[1a,12] This synthesis of 2-X-1-OH's begins with diethyl 2-aminoazulene-1,3-dicarboxylate (**3**) and makes use of four factors: (a) replacement of the amino function by X = Cl, Br, or I (**3** → **4**-X),[12] (b) the ease of nucleophilic displacement of $X:^-$ by $Y:^-$ in **4**,[1a,12] (c) the ability to thermally decarboxylate the azulene-1,3-dicarboxylic acids to the corresponding azulenes,[1,12,13] and (d) the ability of **5** to undergo halogen interchange [**5** (X = Cl) → **5** (X = I)]. Thus we had available



3 **4**



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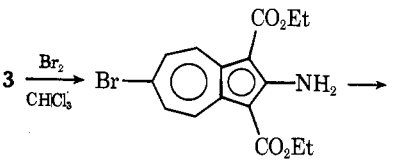
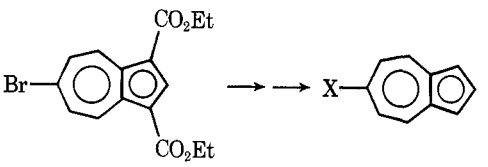
2-substituted azulenes (**5**) where X = CH_3O, CH_3, Cl, Br,[14] and I.[12] Each of these was β-hydroxyethylated (direct method)[5] in high net yield to the respective 2-X-1-OH which were purified by repeated chromatography or (better) by conversion to the 2-X-1-OAc, purification, and hydrolysis to the alcohols. 2-CN-1-OH was prepared by treating 2-I-1-OAc in refluxing DMF with cuprous cyanide in 86% yield followed by hydrolysis to the alcohol.

Thus, the 2-X-1-OH derivatives available are X = CH_3O, CH_3, H, Cl, Br, I, and CN.

Synthesis of 6-Substituted 1-OH's. As pointed out above, the preparation of 6-X-1-OH's also began with amino diester **3** in the Nozoe synthesis. The preparation of this series of compounds was made possible by Nozoe's finding that (a) bromination of **3** proceeds exclusively to diethyl 2-amino-6-bromoazulene-1,3-dicarboxylate (**6**)[12a] and (b) nucleophiles readily replace Br in diethyl 6-bromoazulene-1,3-dicarboxylate (**7**),[15] and our discoveries of (c) the essentially quantitative hydrolysis of dialkyl azulene-1,3-dicarboxylates to their diacids when the esters were dissolved in concentrated sulfuric acid and quenched in water,[16] and (d) a superior method for the protodeamination of **6** → **7**.[17]



6 (97%)



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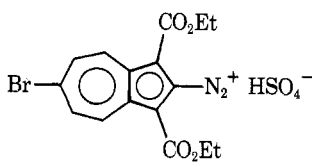
Since bromo diester **7** appeared to be the key compound in the synthesis of a variety of 6-substituted azulenes, efforts were made to optimize the protodeamination of **6**. In a modification of Nozoe's procedure,[15] amine **6** was converted to the purple-blue diazonium salt **8** in dioxane with sulfuric acid and sodium nitrite, the latter dissolved in a small amount of water. Addition of a premixed solution of sulfuric acid and sodium hypophosphite in water gave a 50% yield of **7**. When the diazotization reaction was carried out in the presence of finely ground, suspended sodium hypophosphite a 1:1 mixture of **7** and diethyl 2,6-dibromoazulene-1,3-dicarboxylate (**9**) was isolated. Reduction of **8** with



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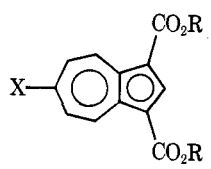

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sodium borohydride[18] gave **7** and **9** in a 1:9 ratio. Use of ethanol as solvent and reducing agent in the diazotization of **6** gave a 26% yield of **7**.

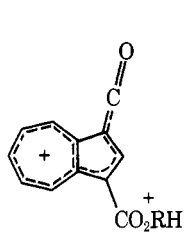
At least two factors contributed to the poor yields of **7**: (1) inefficiency in the reduction of **8** to **7**, and (2) competitive formation of Br^- and attack by this nucleophile at C_2 of **8** leading to dibromide **9**. The susceptibility of the C_6–Br bond of **8** toward nucleophilic displacement has been reported recently by Nozoe.[19]

Our search for a better protodeamination process for the **6** → **7** conversion thus centered on finding conditions involving an in situ reducing agent to be used in a nonaqueous, nonnucleophilic solvent. Orton and Everatt[20a] in 1908 mentioned that *p*-hydroquinone (H_2Q) reduced aryldiazonium salts. We found the H_2Q proved most suitable as the in situ reducing agent in dioxane solvent with isopentyl nitrite and sulfuric acid generating the nitrosating reagent.[17] Since the amine and H_2Q compete for the nitrosating reagent, excesses of H_2Q and alkyl nitrite are required in this in situ protodeamination method. *The yield of purified* **7** *from* **6** *was 93%*. The high efficiency of this protodeamination is also seen in the fact that the deep purple-blue color of intermediate **8** is *not* observed in this reaction. The present procedure[21] should prove to be the method of choice especially where unstable, highly reactive aryldiazonium salts are produced and/or expensive amines are involved.

With bromo diester **7** now available it was possible to proceed to the next step in the synthesis of 6-X-1-OH's. At this point, the ease of displacing Br^- from **7** by various nucleophiles, which was useful in preparing a number of derivatives of diester **10** (R = Et), became a problem when it

came time to remove the 1,3-dicarboethoxy groups to obtain the desired 6-X-azulenes. Nozoe had reported that "mild alkaline treatment of" 7 produced diethyl 6-hydroxyazulene-1,3-dicarboxylate (11);[15] this was readily verified in our work. With 7 and sodium methoxide in methanol, diethyl 6-methoxyazulene-1,3-dicarboxylate (12) was formed in 82% yield; Nozoe had prepared the ethyl ether of 12 in an analogous reaction.[15] When we attempted to saponify 12, the first reaction to occur was formation of the conjugate base of 11.[22] It was obvious at this point that acid hydrolysis conditions would be needed for the conversion of 7 and 12 to their corresponding diacids which might then be decarboxylated to yield 6-bromo- (16) and 6-methoxyazulene (17), respectively.

Considering the structure of diethyl azulene-1,3-dicarboxylate (13) and recalling the classic results of Treffers and Hammett[23] in the esterification–hydrolysis of mesitoic acid and its esters via the acylium ion produced in sulfuric acid, it appeared reasonable that 13 could yield mono- (14) and diacylium ions (15) in strong acid. When 7 and 12 were



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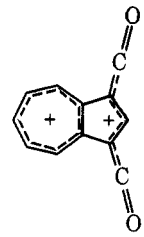

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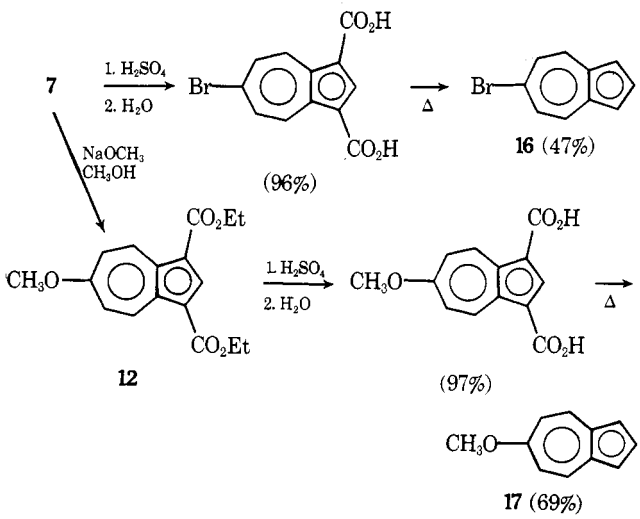
dissolved in concentrated sulfuric acid and these solutions then poured into ice–water, nearly quantitative yields of the corresponding diacids were obtained. Each diacid was then thermally decarboxylated to the respective 6-substituted azulene. When 7 or 13 was dissolved in concentrated sulfuric acid in an NMR tube, the hydrolysis could be followed by NMR spectroscopy. However, only the absorptions of the conjugate acids of the starting esters, intermediate half-esters, and product diacids were observed; 6-Br-14 and 6-Br-15 had been observed previously in SbF_5–FSO_3H–SO_2.[16] The 2–3% water in reagent concentrated sulfuric acid was probably responsible for the different observations in the two media.

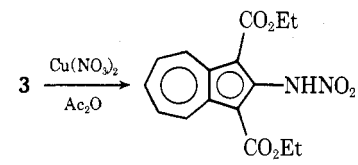


16 and 17 were β-hydroxyethylated (direct)[5] to give the desired 6-Br-1-OH and 6-OCH_3-1-OH in 41% (90% net) and 48% (93% net) yields, respectively. An attempt to carry out Anderson's stepwise β-hydroxyethylation[4] with 16 led to decomposition during the base hydrolysis of 6-bromo-1-azulylacetonitrile.

When 7 was allowed to react with potassium cyanide in ethanol, the sole product isolated was diethyl 6-ethoxyazulene-1,3-dicarboxylate, previously prepared by Nozoe from the reaction of 7 and sodium ethoxide in ethanol.[15] Replacement of Br^- (in 7) by ^-CN was accomplished with cuprous cyanide in DMF at 130 °C giving a 50% yield of diethyl 6-cyanoazulene-1,3-dicarboxylate (18) along with an 18% yield of diethyl 6-dimethylaminoazulene-1,3-dicarboxylate (19).[15] Amine diester 19 must have resulted from partial hydrolysis of the solvent DMF. The chemistry of 18 was not further explored.

6-Cyanoazulene (20) was obtained from the reaction of 16 with cuprous cyanide in DMF in 78% yield. As expected, 20 failed to undergo direct β-hydroxyethylation with 70% of 20 being recovered from the reaction. However, 6-CN-1-OAc was obtained from the reaction of 6-Br-1-OAc with cuprous cyanide in DMF. Base hydrolysis of 6-CN-1-OAc produced 6-CN-1-OH.

Since bromination of 3 had proceeded smoothly to yield 6 which ultimately was converted into 6-Br-1-OH, a successful nitration of 3 could conceivably produce 6-NO_2-1-OH. While tetranitromethane in pyridine[9] gave no reaction with 3, the reaction of 3 and cupric nitrate in acetic anhydride[6,8a,9] produced a base-soluble product. Elemental and spectral analysis of this acidic compound established that it was not the expected C-nitration product, 6-NO_2-3, but rather the isomeric product of N-nitration, diethyl 2-nitroaminoazulene-1,3-dicarboxylate (21).



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We[24] had previously prepared 6-methylazulene by a modification of the Ziegler–Hafner azulene synthesis.[25] Direct β-hydroxyethylation[5] of 6-methylazulene gave 6-CH_3-1-OH along with a small amount of 2,2′-(6-methyl-1,3-azulene)diethanol, the latter structure assigned on the basis of its NMR spectrum.

The 6-X-1-OH (or acetate) derivatives prepared in this study were X = CH_3O, CH_3, H, Br, and CN.

Preparation of the Tosylate Esters. In general, the tosylate esters of the above derivatives of 1-OH were prepared by treating the alcohol in ether at 0 °C with freshly sublimed *p*-toluenesulfonyl chloride and crushed potassium hydroxide.[26] It was believed that this procedure would "ensure" the structural integrity of certain of the more reactive substrates during this derivatization. Certain of the tosylates were oily liquids and were routinely converted to their *sym*-trinitrobenzene (TNB) complexes for analysis and storage; in several cases, the TNB complexes were stable to storage for months in the refrigerator while the uncomplexed, liquid tosylates decomposed after short periods of time.

Substituent Effects on λ_{max} in the Visible Region of Azulenes. While the major emphasis of this synthetic work was to prepare substituted 2-(1-azulyl)ethyl tosylates for solvolytic studies, it is of interest to observe the substituent effects on the λ_{max} in the visible spectra of these azulene derivatives. We have a number of various types of substituents on the azulene ring 2, 3, and 6 positions, and their shifts ($\Delta\lambda_{max}$) as well as those of the related monosubstituted azulenes are listed in Table I.

The small changes in λ_{max} seen in going from 1-OH (596 nm) to 1-OAc (593 nm) to 1-OTs (590 nm) in CH_2Cl_2 solvent appear to be real since the same trend is noted in all

Table I. Comparison of Substituent Effects on the Visible λ_{max} of 1-OH, 1-OAc, and 1-OTs and Related Monosubstituted Azulenes

	$\Delta\lambda_{max}$, nm[a,i]		$\Delta\lambda_{max}$, nm[b]	Ref
2-CH_3O-1	−60 ± 1 (3)[c]	2-CH_3O-Az	−57	*i*, 12a
2-CH_3-1	−18 ± 2 (2)	2-CH_3-Az	−18[g]	*i*
2-Cl-1	−30 ± 2 (2)	2-Cl-Az	−29	*j*, 12a
2-Br-1	−28 ± 1 (3)	2-Br-Az	−23	*i*
2-I-1	−18 (1) [d,e]	2-I-Az	−20	*j*, 12a
2-NC-1	53 ± 2 (3)	2-NC-Az	55	12a
3-CH_3O-1	101 ± 2 (2)	1-CH_3O-Az	104	*i*, 11
3-CH_3-1	29 ± 1 (2)	1-CH_3-Az	28	4
3-CH_3S-1	22 ± 1 (2)	1-CH_3S-Az	1	7
3-Br-1	17 ± 2 (2)	1-Br-Az	25	8a
3-NCS-1	−20 ± (1)[d,f]	1-NCS-Az	−27[h]	6
3-CH_3CO-1	−38 ± 1 (2)	1-CH_3CO-Az	−30	8a
3-NC-1	−34 (1)	1-NCAz	−24	*k*, *l*
3-O_2N-1	−65 ± 2 (3)	1-O_2N-Az	−48	8a
6-CH_3O-1	−53 ± 2 (2)	6-CH_3O-Az	−47	*m*, *n*
6-CH_3-1	−15 (1)	6-CH_3-Az	−15	*m*, *n*
6-Br-1	6 ± 1 (2)	6-Br-Az	2	*m*
6-NC-1	62 ± 1 (3)	6-NC-Az	51	*m*

[a] λ_{max} (X-1) − λ_{max} (1); λ_{max} 1-OH (596 nm), 1-OAc (593 nm), 1-OTs (590 nm) in CH_2Cl_2. Polar solvent (CH_2Cl_2 and 95% EtOH) used except where noted. [b] λ_{max} (X-Az) − λ_{max} (Az-H); λ_{max} Az-H (580 nm in cyclohexane, 578 nm in CH_2Cl_2 or EtOH). Nonpolar solvent (cyclohexane and *n*-hexane) used except where noted. [c] Number of O-derivatives of 1-OH used; contains tosylates λ_{max} except where noted. [d] ROAc. [e] Solvent cyclohexane. [f] Solvent CCl_4. [g] Solvent CH_2Cl_2. [h] Solvent $CHCl_3$. [i] This work. [j] J. M. Richmond, Ph.D. Thesis, Kansas State University, 1974. [k] D. J. Gale, Ph.D. Thesis, University of Washington, 1957. [l] K. Hafner and C. Bernhard, *Justus Liebigs Ann. Chem.*, **625**, 108 (1959). [m] H. E. Petty, Ph.D. Thesis, Kansas State University, 1971. [n] K. Hafner and K-D. Asmus, *Justus Liebigs Ann. Chem.*, **671**, 31 (1964).

other series of these ring-substituted derivatives.

Overall, the additivity of the substituent effects holds very well. This is especially true with the 2-substituted derivatives of 1-OH, 1-OAc, and 1-OTs.

In the 3- and 6-substituted derivatives of 1, larger hypsochromic shifts are observed for the electron-withdrawing ring substituents compared to those measured for the corresponding monosubstituted azulenes (X-Az). This we attribute primarily to a solvent effect on λ_{max} where the effect is attenuated in the nonpolar solvent. This is amply demonstrated with 3-NC-1-OTs, λ_{max} 552 nm (95% EtOH), compared to 3-NC-1-OAc, λ_{max} 575 nm (cyclohexane).

The case of the 3-thiomethyl derivatives, 3-CH_3S-1, appears to be the most glaring inconsistency in the additivity of substituent effects on λ_{max} in Table I. We doubt that this magnitude of change ($\Delta\Delta\lambda_{max}$ = 21 nm) is due to a solvent effect since none is observed with 3-CH_3O-1 (CH_2Cl_2) vs. 1-CH_3O-Az (cyclohexane). It must be noted that absorption fine structure seen in cyclohexane is lost in CH_2Cl_2 solvent.

The reported visible spectrum of 1-thiomethylazulene (1-CH_3S-Az) in cyclohexane has three maxima of essentially identical intensities, 581 nm (ϵ 269), 599 (268), 627 (265), and 695 (141).[7] The above evidence and the fact that 1,3-bis(thiomethyl)azulene has $\Delta\lambda_{max}$ 47 nm (cyclohexane) leads us to conclude that the 599-nm maximum in 1-CH_3S-Az is the band to be associated with the 1-thiomethyl group when using the empirical Plattner's rules for predicting the visible spectra of substituted azulenes; for 1-CH_3S–, $\Delta\lambda_{max}$ is 19 nm.[29]

Experimental Section[27]

2-(1-Azulyl)ethanol (1-OH). A. Stepwise Construction of Side Chain.[4] The method of Anderson et al.[4] was used with certain modifications; relevant spectral data are included. 1-Azulylmethyltrimethylammonium iodide was obtained in 84% yield as purple needles: mp >230 °C; NMR (CD_3CN, internal Me_4Si) τ 1.0–2.8 (m, Az-H's, 7), 5.00 (s, CH_2, 2), and 6.90 (s, CH_3's, 9); uv–visible (95% EtOH) 649 nm (log ϵ 2.12), 591 (2.55), 554 (2.62), 351 (3.58), 336 (3.74), 328 (3.63), 287 (4.27), 282 (4.71), and 277 (4.76).

From 450 mg of the above quaternary iodide and 260 mg of KCN in 20 ml of absolute ethanol, we obtained 216 mg (95%) of 1-azulylacetonitrile: mp 54–55 °C (lit.[4] 43–44 °C); NMR (CCl_4, internal Me_4Si) τ 1.6–3.2 (m, Az-H's, 7) and 6.10 (s, CH_2, 2); uv–visible (CH_2Cl_2) 616 nm (log ϵ 2.51), 581 (2.55), 355 (3.44), 341 (3.66), 286 (4.62), 282 (4.67), and 277 (4.70).

Forty milliliters of a 0.6 M solution of potassium hydroxide in 50% aqueous ethanol was swept with N_2 for 2 h. To this solution heated under reflux was added 100 mg (0.6 mmol) of 1-azulylacetonitrile in 2 ml of THF and the mixture was heated under reflux for 7 h with a continuous, slow N_2 sweep. The solution was allowed to cool and 50 ml of water and 100 ml of ether were added. The layers were separated to remove a small trace of ether-soluble material. The aqueous layer was acidified with 5% hydrochloric acid and extracted with two 100-ml portions of ether. The combined ether layers were washed twice with equal volumes of water and dried ($MgSO_4$). The solvent was evaporated to afford 95 mg (86%) of 1-azulylacetic acid as a blue oil which crystallized as blue needles: mp 89.9–91.0 °C (lit.[4] 92–93 °C); ir (CCl_4) 3.0–3.3 (OH) and 5.85 μ (C=O); NMR (CCl_4, internal Me_4Si) τ −1.90 (s, OH, 1), 1.6–3.3 (m, Az-H's, 7), and 6.07 (s, CH_2, 2); uv–visible (CH_2Cl_2) 691 nm (log ϵ 2.05), 630 (2.47), 586 (2.53), 356 (3.43), 341 (3.67), 332 (3.53), 288 (4.64), 283 (4.70), and 277 (4.72).

Reduction of 150 mg of 1-azulylacetic acid with diborane gave 125 mg (90%) of 1-OH: mp 57–58 °C (lit.[4] 59–60 °C); ir (neat film) 2.95 (OH) and 9.63 μ (C–O); NMR (CCl_4, internal Me_4Si) τ 1.4–3.4 (m, Az-H's, 7), 6.26 (t, α-CH_2, 2), 6.86 (t, β-CH_2, 2), and 7.36 (s, OH, 1); uv–visible (CH_2Cl_2) 704 nm (log ϵ 1.93), 646 (2.39), 596 (2.46), 359 (3.32), 343 (3.63), 288 (4.58), 283 (4.67), and 278 (4.70); mass spectrum (70 eV, heated inlet) *m/e* (rel intensity) 172 (19, $M^{\cdot+}$), 141 (100), and 115 (16).

B. Direct β-Hydroxyethylation of Azulene.[5] The procedure utilizes ethylene oxide, azulene, and $AlCl_3$ in CH_2Cl_2. The major product is 1-OH along with a small amount of 1,3-bis(2-hydroxyethyl)azulene which are readily separated by chromatography on alumina.[5]

2-(1-Azulyl)ethyl Acetate (1-OAc). To 90 mg (0.52 mmol) of 1-OH dissolved in 3.0 ml of dry pyridine and cooled to 0 °C was added 0.6 ml of reagent grade acetic anhydride and the mixture was allowed to stir at 0 °C for 2 h. A mixture of 25 ml of ice-cold water and 10 ml of 5% hydrochloric acid was added and all of the blue color was extracted with three 20-ml portions of CH_2Cl_2. The combined organic layers were washed three times with ice-cold 5% hydrochloric acid and once with 100 ml of cold water, and dried ($MgSO_4$). The solvent volume was reduced and the residue was chromatographed on alumina[28] where CH_2Cl_2 eluted 103 mg (92%) of the acetate as a blue oil: ir (neat film) 5.70 (C=O) and 9.55 μ (C–O); NMR (CCl_4, internal Me_4Si) τ 1.6–3.3 (m, Az-H's, 7), 5.76 (t, α-CH_2, 2), 6.76 (t, β-CH_2, 2), 8.13 (s, CH_3, 3); uv–visible (CH_2Cl_2) 643 nm (log ϵ 2.41), 593 (2.49), 357 (3.38), 343 (3.67), 288 (4.60), 283 (4.70), and 278 (4.73); mass spectrum (70 eV, heated inlet) *m/e* (rel intensity) 214 (20, $M^{\cdot+}$), 154 (78), and 141 (100).

To 140 mg (0.66 mmol) of the acetate was added 150 mg (0.70 mmol) of TNB in 5.0 ml of ethyl acetate. The solvent volume was reduced in half and this mixture was added to a solution of 1.0 ml of ethyl acetate in 7.0 ml of hexane. The solution was cooled and the complex crystallized as large violet plates (172 mg, 62%). Repeated recrystallization afforded an analytical sample, mp 94.7–94.9 °C.

Anal. Calcd for $C_{20}H_{17}N_3O_8$: C, 56.21; H, 4.01. Found: C, 56.19; H, 3.84.

2-(1-Azulyl)ethyl Tosylate (1-OTs). To a solution of 115 mg (0.67 mmol) of 1-OH dissolved in 3.5 ml of dry ether and cooled to 0 °C was added 40 mg (0.61 mmol) of powdered KOH followed by 130 mg (0.70 mmol) of *p*-toluenesulfonyl chloride. The mixture was allowed to stir at 0 °C for 5 h and then 20 ml of ice-cold water and 20 ml of ether were added. The layers were separated, the ether solution was dried (K_2CO_3), and the solvent volume was reduced. The residue was immediately chromatographed on deactivated (7% H_2O) alumina[28] where CH_2Cl_2 eluted a blue band which afforded 155 mg of crude tosylate as an unstable blue oil upon solvent volume reduction.

The crude tosylate was dissolved in 5.0 ml of ethyl acetate containing 150 mg (0.70 mmol) of TNB. The solvent volume was reduced in half, 3.0 ml of hexane was added, and the solution was

cooled to freezer temperature. Large brown crystals (175 mg, 67%) were formed upon standing: mp 76.4–76.7 °C; ir (neat film) 6.15 (aryl C–C), 7.47 (S–O_{asym}), and 8.50 μ (S–O_{sym}); NMR ($CDCl_3$, internal Me_4Si) τ 0.60 (s, TNB-H's, 3), 1.4–3.2 (m, azulyl and tosyl H's, 11), 5.66 (t, α-CH_2, 2), 6.56 (t, β-CH_2, 2), and 7.56 (s, CH_3, 3); uv–visible (CH_2Cl_2) 701 nm (log ϵ 2.03), 637 (2.45), 590 (2.52), 357 (3.42), 342 (3.70), 333 (3.56), 288 (4.63), 283 (4.70), and 278 (4.73); mass spectrum (20 eV, heated inlet) *m/e* (rel intensity) 326 (20, $M\cdot^+$), 154 (58), and 141 (100).

Anal. Calcd for $C_{25}H_{21}N_3O_9S$: C, 55.65; H, 3.92. Found: C, 55.41; H, 4.02.

1-Azulyl Benzoate.[11] To a solution of 1.00 g (7.83 mmol) of azulene in 50 ml of CCl_4 was added 945 mg (3.91 mmol) of recrystallized benzoyl peroxide. The mixture was heated under reflux with a dry, oxygen-free, nitrogen atmosphere for 2.5 h. The solvent volume was reduced, and the residue chromatographed on Florisil (Fisher, 60–100 mesh). Elution with hexane afforded a violet band of unreacted azulene, 500 mg. CCl_4 eluted a narrow, blue band and a faint, green band, neither of which was further investigated, and finally a broad, blue band. CH_2Cl_2 eluted a green band.

The broad, blue band gave 291 mg (15%, 30% net) of the title compound, mp 61.0–62.0 °C (lit.[11] mp 62.5–63.5 °C). (See paragraph at end of paper regarding supplementary material.)

The green band afforded 300 mg (10%, 20% net) of 1,3-azulene dibenzoate. Crystallization from ether yielded green crystals: mp 129.5–130.5 °C (lit.[11] mp 132–134 °C); ir (KBr) 5.75 μ (s, C=O); NMR ($CDCl_3$, internal Me_4Si) τ 1.56–2.13 (m, 6) and 2.20–3.33 (m, 10).

Anal. Calcd for $C_{24}H_{16}O_4$: C, 78.25; H, 4.38. Found: C, 78.23; H, 4.72.

1-Methoxyazulene. The preparation of 230 mg of this compound was accomplished in 70% yield by the method of Replogle[11] from 516 mg (2.08 mmol) of 1-azulyl benzoate, 10 ml of methyl iodide, and 10 ml of 1.9 M methanolic sodium hydroxide in 100 ml of dry (BaO) DMF under a nitrogen atmosphere for 6 h at room temperature. The emerald-green oil crystallized from hexane as green needles, mp 29.5–30.0 °C (lit.[11] mp 26–28 °C). (See paragraph at end of paper regarding supplementary material.)

For analysis a TNB complex was prepared and crystallized from 1:1 CH_2Cl_2–hexane to afford long, fine, black needles, mp 134.0–135.0 °C.

Anal. Calcd for $C_{17}H_{13}O_7N_3$: C, 54.99; H, 3.53. Found: C, 54.94; H, 3.63.

2-(3-Methoxy-1-azulyl)ethanol (3-CH_3O-1-OH). A mixture of 153 mg (1.5 mmol) of *N,N,N',N'*-tetramethyldiaminomethane, 30 mg (1.0 mmol) of paraformaldehyde, and 4 ml of acetic acid was heated to develop a clear solution. This solution, cooled to room temperature, was added dropwise with stirring to 225 mg (1.42 mmol) of 1-methoxyazulene in 20 ml of CH_2Cl_2 at 0 °C. This mixture was allowed to stir for 1 h at 0 °C, placed in the refrigerator overnight, and then diluted with 100 ml of CH_2Cl_2, washed with three 100-ml portions of water, and dried (Na_2SO_4), the solvent volume was reduced, and the green residue was chromatographed on alumina.[28] CH_2Cl_2 eluted a yellow band that was not investigated, and developed a broad, blue band which was eluted with anhydrous ether. The solvent volume of the blue eluate was reduced, and the residue, dissolved in 10 ml of absolute ethanol, treated with an excess of methyl iodide. Crystallization afforded 269 mg (53%) of the quaternary iodide, as green crystals: mp >300 °C; ir (KBr) no characteristic absorptions; λ_{max} (95% ethanol) 286 nm (log ϵ 4.61), 360 (3.62), 377 (3.62), and 697 (2.88).

Anal. Calcd for $C_{15}H_{20}ONI$: C, 50.43; H, 5.64. Found: C, 50.20; H, 5.70.

To 269 mg (0.755 mmol) of quaternary ammonium iodide (above) in 25 ml of absolute ethanol was added 145 mg (2.40 mmol) of KCN. The mixture was heated under reflux for 50 min, diluted with 100 ml of water, and extracted with 50 ml of ether. The ethereal layer was washed with two 50-ml portions of water and dried (Na_2SO_4), the solvent volume was reduced, and the green residue was chromatographed on basic alumina.[28] CH_2Cl_2 eluted a broad, blue band followed by a brown band. Continued elution with $CHCl_3$ developed a narrow, blue band. Only the first, blue band was examined, which afforded 115 mg (78%) of 3-methoxy-1-azulylacetonitrile. Crystallization from CCl_4 gave green needles, mp 81.8–82.0 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{13}H_{11}ON$: C, 79.16; H, 5.62; N, 7.10. Found: C, 78.89; H, 5.49; N, 6.82.

Following the above procedure (a) in the preparation of 1-OH, 175 mg of the above nitrile in 20 ml of THF was hydrolyzed with base for 18 h under reflux and an N_2 atmosphere. Work-up gave 160 mg (83%) of 3-methoxy-1-azulylacetic acid, mp 115–118 °C. (See paragraph at end of paper regarding supplementary material.)

Sodium borohydride (220 mg, 5.8 mmol) was added to a solution of 160 mg (0.74 mmol) of 3-methoxy-1-azulylacetic acid in 20 ml of dry tetrahydrofuran. When the evolution of hydrogen had ceased, a solution of 3 ml of boron trifluoride etherate in 20 ml of dry tetrahydrofuran was added dropwise over a period of 10–15 min to the stirred mixture. The green mixture was stirred for 1.5 h as the color gradually changed to blue. The mixture was then acidified by the dropwise addition of 20 ml of 10% hydrochloric acid, diluted with 100 ml of water, and extracted with two 100-ml portions of ether. The combined ethereal layers were washed with a 100-ml portion of water. The extracts were dried (Na_2SO_4), the solvent volume reduced, and the residue chromatographed on alumina[28] where $CHCl_3$ eluted a single, blue band, which afforded 145 mg (97%) of 3-CH_3O-1-OH, an emerald-green oil. (See paragraph at end of paper regarding supplementary material.)

For analysis a TNB complex was prepared and crystallized from 1:1 ethyl acetate–hexane to yield brown needles: mp 147.0–148.0 °C; ir (KBr) 3.05 (m, O–H) and 9.60 μ (m, C–O); λ_{max} (CH_2Cl_2) 291 nm (log ϵ 4.62), 362 (3.68), 378 (3.64), 695 (2.52), and 770 (2.44) (sh).

Anal. Calcd for $C_{19}H_{17}O_8N_3$: C, 54.94; H, 4.13. Found: C, 54.99; H, 4.26.

2-(3-Methoxy-1-azulyl)ethyl Tosylate (3-CH_3O-1-OTs). 3-CH_3O-1-OH (145 mg, 0.72 mmol) was converted to its tosylate ester by the method described for 1-OTs. After work-up, the residue was chromatographed on deactivated (4.6% water) basic alumina[28] with CH_2Cl_2. A blue band was eluted affording 230 mg (90%) of 3-CH_3O-1-OTs as a green oil.

This rather unstable tosylate was converted to its TNB complex which was obtained as long, black needles, mp 98.5–99.5 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{26}H_{23}O_{10}N_3S$: C, 54.83; H, 4.07; N, 7.38. Found: C, 54.55; H, 4.12; N, 7.52.

2-(3-Methyl-1-azulyl)ethanol (3-CH_3-1-OH). To a solution of 200 mg (1.16 mmol) of 1-OH in 10 ml of CH_2Cl_2 and 10 ml of acetic acid, cooled to 0 °C, was added 135 mg (1.32 mmol) of *N,N,N',N'*-tetramethylmethylenediamine dissolved in 4 ml of acetic acid. This mixture was stirred at 0 °C for 2 h, diluted with 50 ml of ice-cold water and 50 ml of 5% hydrochloric acid, and extracted with 50 ml of ether. The aqueous layer was neutralized with dilute potassium hydroxide and extracted with two 100-ml portions of ether. The combined extracts were dried (K_2CO_3), the solvent volume reduced, and the residue dissolved in 4 ml of absolute ethanol and cooled to 0 °C. To this solution was added 3 ml of methyl iodide. Crystallization afforded 375 mg (87%) of the ammonium salt.

To a solution of 375 mg (1.01 mmol) of the ammonium salt in 20 ml of absolute ethanol was added 60 mg (1.59 mmol) of $NaBH_4$ and the mixture was allowed to stir at room temperature for 10 h. A 1-ml aliquot of the mixture added to 1 ml of ether and 2 ml of water yielded a violet color in the aqueous layer, indicating incomplete conversion. The reaction mixture was then heated at reflux for 7 min, diluted with 100 ml of water, and extracted with three 100-ml portions of ether. The combined extracts were dried (K_2CO_3), the solvent volume reduced, and the residue chromatographed on deactivated (6% water) basic alumina[28] with acid-free (alumina) benzene. A broad, blue band eluted that was followed closely by a second blue band that was not investigated. The first blue band afforded 95 mg (51%) of 3-CH_3-1-OH as a blue oil that was unstable in the presence of trace amounts of acid. (See paragraph at end of paper regarding supplementary material.)

For analysis a TNB complex was prepared and crystallized from 1:1 ethyl acetate–hexane. Two recrystallizations afforded fine, long brown needles: mp 135.5–136.5 °C; ir (KBr) 3.08 (m, O–H) and 9.58 μ (m, C–O); λ_{max} (95% ethanol) 281 nm (log ϵ 4.76), 334 (3.55) (sh), 349 (3.76), 365 (3.63), 625 (2.50), 660 (2.43) (sh), 685 (2.40), and 765 (1.95).

Anal. Calcd for $C_{19}H_{17}O_7N_3$: C, 57.14; H, 4.29; N, 10.52. Found: C, 57.36; H, 4.15; N, 10.45.

2-(3-Methyl-1-azulyl)ethyl Tosylate (3-CH_3-1-OTs). The tosylate ester was prepared from 95 mg of 3-CH_3-1-OH by the method for 1-OTs. Chromatography on deactivated (4.6% H_2O) alumina[28] with acid-free (Al_2O_3) CH_2Cl_2 eluted a single band affording 167 mg (96%) of 3-CH_3-1-OTs.

This unstable tosylate was dissolved in 1.5 ml of ethyl acetate containing 107 mg (0.50 mmol) of TNB. An equal volume of hexanes was added and the solution cooled to afford brown-violet nee-

dles of the title compound, mp 81.0–81.5 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{26}H_{23}O_9N_3S$: C, 56.41; H, 4.19. Found: C, 56.70; H, 4.05.

2-(3-Thiocyano-1-azulyl)ethyl Acetate (3-SCN-1-OAc). A solution of 35 mg (0.16 mmol) of 1-OAc in 5 ml of CCl_4 was cooled to 0 °C. To this mixture was added a solution of thiocyanogen[6] (100 mg of lead thiocyanate in 5.0 ml of CCl_4 and Br_2 added to yield a residual red color which was removed with 10 mg more of lead thiocyanate and filtered) and the resulting mixture was allowed to stir at 0 °C for 3 h. This solution was then poured onto a column of basic alumina[28] where CH_2Cl_2 eluted 38 mg (89%) of the title compound as a blue-violet solid which afforded long violet needles upon recrystallization from CH_2Cl_2–hexane, mp 94.2–94.4 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{15}H_{13}NO_2S$: C, 66.40; H, 4.83. Found: C, 66.55; H, 4.96.

2-(3-Methylthio-1-azulyl)ethyl Acetate (3-CH_3S-1-OAc). A solution of 24 mg (0.09 mmol) of 3-SCN-1-OAc dissolved in 5.0 ml of methanol was cooled to 0 °C. The solution was continually swept with O_2-free nitrogen gas. To this solution was added 1.0 ml of methyl iodide (excess) and 100 mg (1.78 mmol) of potassium hydroxide in 5.0 ml of 50% aqueous methanol, and the solution was allowed to stir at 0 °C for 2 h. A mixture of 30 ml of ice-cold water and 50 ml of ether was added and the layers were separated. The aqueous layer was again extracted with 50 ml of ether to remove the last trace of blue color. The combined ether layers were washed with three 50-ml portions of cold water and dried ($MgSO_4$). The solvent volume was reduced and the residue was chromatographed on alumina[28] where $CHCl_3$ eluted 16 mg (84%) of 3-CH_3S-1-OH as an unstable, green oil. (See paragraph at end of paper regarding supplementary material.)

The crude 3-CH_3S-1-OH (77 mg, 0.35 mmol) was then acetylated with acetic anhydride in pyridine at 0 °C. After normal workup, the acetate was chromatographed on alumina[28] where CH_2Cl_2 eluted 81 mg (88%) of 3-CH_3S-1-OAc as a green oil which crystallized on standing, mp 39.2–40.0 °C. (See paragraph at end of paper regarding supplementary material.)

To 60 mg (0.23 mmol) of 3-CH_3S-1-OAc dissolved in 3.0 ml of ethyl acetate to which had been added 90 mg (0.42 mmol) of TNB, an equal volume of hexanes was added and this solution was placed in a refrigerator where crystallization afforded 65 mg (61%) of long, brown-black needles, mp 85.6–85.8 °C.

Anal. Calcd for $C_{21}H_{19}N_3O_8S$: C, 53.27; H, 4.04. Found: C, 53.21; H, 4.01.

2-(3-Methylthio-1-azulyl)ethyl Tosylate (3-CH_3S-1-OTs). 3CH_3S-1-OH (70 mg, 0.32 mmol) was converted to its tosylate ester by the method given for 1-OTs. Chromatography on deactivated (6% H_2O) alumina[28] developed a blue band of the tosylate which eluted with CH_2Cl_2. Evaporation of the solvent gave the tosylate as a green, unstable oil.

The tosylate ester was converted to its TNB complex which crystallized as long, black needles, 175 mg (94%). Recrystallization was repeated several times to afford an analytical sample, mp 98.2–98.4 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{26}H_{23}N_3O_9S_2$: C, 53.33; H, 3.96. Found: C, 53.31; H, 3.97.

2-(3-Bromo-1-azulyl)ethyl Acetate (3-Br-1-OAc). To a solution of 25 mg (0.11 mmol) of 1-OAc in 3.0 ml of dry benzene was added 25 mg (0.14 mmol) of *N*-bromosuccinimide and the mixture was allowed to stir for 2 min at room temperature. This solution was poured onto a column of alumina[28] where CH_2Cl_2 eluted a blue band which afforded 33 mg (96%) of 2-(3-bromo-1-azulyl)ethyl acetate as a green oil: ir (neat film) 5.72 μ (C=O); NMR (CCl_4, internal Me_4Si) τ 1.6–3.2 (m, Az-H's, 6), 5.73 (t, α-CH_2, 2), 6.67 (t, β-CH_2, 2), 7.97 (s, CH_3, 3).

3-Br-1-OAc (66 mg, 0.23 mmol) was converted to its TNB complex which crystallized as long, brown needles (75 mg, 83%). Repeated recrystallizations from ethyl acetate–hexane afforded an analytical sample: mp 84.7–85.1 °C; uv–visible (CH_2Cl_2) 609 nm (log ϵ 2.58), 364 (3.80), 348 (3.84), 340 (3.74), 295 (4.73), and 285 (4.78).

Anal. Calcd for $C_{20}H_{16}N_3BrO_8$: C, 47.45; H, 3.19. Found: C, 47.46; H, 3.11.

2-(3-Bromo-1-azulyl)ethyl Tosylate (3-Br-1-OTs). To 100 mg (0.20 mmol) of 3-Br-1-OAc·TNB complex dissolved in a mixture of 4.0 ml of ethanol, 2.0 ml of THF, and 0.5 ml of water was added 0.30 g (5.4 mmol) of KOH and the solution was cooled to 0 °C. The mixture was allowed to stir at 0 °C for 1 h and then 100 ml of ice-cold water and 50 ml of ether were added. The layers were separated and ether extraction of the aqueous layer was repeated. The combined ether layers were washed with two 50-ml portions of ice-cold water and dried ($MgSO_4$), and the solvent volume was reduced. The residue was chromatographed on alumina[28] where $CHCl_3$ eluted 35 mg (88%) of 3-Br-1-OH as an unstable, green oil. (See paragraph at end of paper regarding supplementary material.)

3-Br-1-OH (35 mg, 0.14 mmol) was converted to its tosylate ester by the method given for 1-OTs. It was chromatographed on deactivated (6% H_2O) alumina[28] where CH_2Cl_2 eluted it as a blue band affording 61 mg of crude 3-Br-1-OTs. The tosylate was added to 2.0 ml of ethyl acetate containing 60 mg (0.28 mmol) of TNB. An equal volume of hexanes was added and the mixture was cooled. Brown-pink crystals formed after 3 h to afford 61 mg (72%) of the complex. This sample was recrystallized several times from ethyl acetate–hexane, mp 86.5–86.6 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{25}H_{20}BrN_3O_9$: C, 48.55; H, 3.26. Found: C, 48.74; H, 3.28.

2-(3-Acetyl-1-azulyl)ethyl Acetate (3-CH_3CO-1-OAc). To a solution of 35 mg (0.16 mmol) of 1-OAc in 3.0 ml of dry nitrobenzene was added 0.6 ml of reagent grade acetic anhydride followed by 3 drops of stannic chloride. The solution was allowed to stir for 7 min at room temperature and then a mixture of 20 ml of ice-cold water and 20 ml of CCl_4 was added. The layers were separated and the CCl_4 extraction on the aqueous layer was repeated. The combined organic layers were washed with three 20-ml portions of water and dried ($MgSO_4$). The solution was filtered directly onto a column of alumina[28] where elution with $CHCl_3$ afforded 36 mg (86%) of the acetate as a lavendar oil: ir (neat film) 5.71 (ester C=O) and 6.03 μ (ketone C=O).

To 42 mg (0.16 mmol) of 3-CH_3CO-1-OAc dissolved in 2.0 ml of ethyl acetate was added 60 mg (0.28 mmol) of TNB. An equal volume of hexanes was added and the solution was cooled to induce crystallization. The complex (61 mg, 79%) crystallized as long, red-brown needles and was crystallized several more times, mp 93.2–93.5 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{22}H_{19}N_3O_9$: C, 56.21; H, 4.08. Found: C, 56.10; H, 4.11.

2-(3-Acetyl-1-azulyl)ethyl Tosylate (3-CH_3CO-1-OTs). 3-CH_3CO-1-OAc (50 mg, 0.19 mmol) was hydrolyzed to 3-CH_3CO-1-OH in quantitative yield as per 3-Br-1-OAc → 3-Br-1-OH conditions. $CHCl_3$ eluted 3-CH_3CO-1-OH from alumina[28] chromatography as an unstable, green semisolid. (See paragraph at end of paper regarding supplementary material.)

3-CH_3CO-1-OH (88 mg, 0.41 mmol) was converted to its tosylate ester by the method given for 1-OTs. It was chromatographed on alumina[28] where CH_2Cl_2 eluted it as a purple band giving 90 mg (53%) of 3-CH_3CO-1-OTs as long, green needles, mp 91.7–92.0 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{21}H_{20}O_4S$: C, 68.45; H, 5.47. Found: C, 68.47; H, 5.61.

2-(3-Cyano-1-azulyl)ethyl Acetate (3-CN-1-OAc). Method A. A mixture of 250 mg (0.85 mmol) of 3-Br-1-OAc and 114 mg (1.28 mmol) of CuCN in 10 ml of dry DMF was heated at 135 °C for 10 h under an N_2 atmosphere. The mixture was cooled, diluted with 100 ml of benzene, and washed with six 100-ml portions of warm, aqueous NaCN (prepared from 600 ml of warm water and 20 g of NaCN). The organic layer was washed with 100 ml of water and dried (Na_2SO_4), the solvent volume reduced, and the residue chromatographed on alumina.[28] Elution with 1:1 CCl_4–CH_2Cl_2 developed a blue band that afforded 150 mg (60% recovery) of unreacted 3-Br-1-OAc. Continued elution with CH_2Cl_2 yielded a violet band that afforded 65 mg (32%, 80% net) of 3-CN-1-OAc. Crystallization from CCl_4 afforded violet crystals, mp 57.0–57.5 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{15}H_{13}O_2N$: C, 75.29; H, 5.48. Found: C, 75.08; H, 5.49.

Method B. Stannic chloride (3.48 g, 13.3 mmol) was added to 1.410 g (13.3 mmol) of BrCN with cooling and stirring under an N_2 atmosphere. A white suspension appeared, and the mixture was stirred at room temperature for 10 min. To this mixture was added dropwise 285 mg (1.33 mmol) of 1-OAc in 20 ml of dry ether, and the mixture allowed to stir at room temperature for 18 h. The mixture was diluted with 50 ml of 5% hydrochloric acid and extracted

with three 50-ml portions of $CHCl_3$. The combined, blue extracts were washed with 50 ml of 5% aqueous sodium bicarbonate which was accompanied by a color change to forest green. The extracts were washed with 50 ml of water and dried (Na_2SO_4), the solvent volume reduced, and the residue chromatographed on basic alumina[28] with 1:1 CCl_4–CH_2Cl_2. A blue band eluted that was followed by a yellow-green band. Further elution with CH_2Cl_2 yielded a violet band and $CHCl_3$ afforded a dark-green band. Only the violet band, that afforded 60 mg (19%) of the title compound, was investigated. The NMR and ir spectra were identical with those obtained from method A.

2-(3-Cyano-1-azulyl)ethyl Tosylate (3-CN-1-OTs). 3-CN-1-OAc (125 mg, 0.57 mmol) was hydrolyzed to 3-CN-1-OH as per the 3-Br-1-OAc → 3-Br-1-OH conditions. The alcohol was chromatographed on alumina[28] where $CHCl_3$ eluted it as a violet band which afforded 110 mg (99%) of 3-CN-1-OH as a violet oil. (See paragraph at end of paper regarding supplementary material.)

A TNB complex was prepared in the usual way and recrystallized from 1:1 ethyl acetate–hexane giving red-brown plates, mp 84.0–84.5 °C. Examination of the NMR spectrum of this derivative revealed it to be a 2:1 complex, 3-CN-1-OH–2TNB; TNB complexes of azulenes in other than 1:1 ratios are known.[29] The log ϵ values below are calculated assuming a 2:1 complex ratio: λ_{max} (CH_2Cl_2) 285 nm (log ϵ 4.54), 290 (4.65), 295 (4.60), 302 (4.74), 344 (3.71), 354 (3.80), 371 (3.92), 563 (2.63), 604 (2.57) (sh), and 665 (2.11) (sh).

3-CN-1-OH (110 mg, 0.56 mmol) was converted to its tosylate ester by the method given for 1-OTs. It was chromatographed on deactivated (6% H_2O)[28] alumina where CH_2Cl_2 eluted it as a violet band giving 175 mg (89%) of 3-CN-1-OTs as violet needles, mp 111.0–111.5 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{20}H_{17}O_3NS$: C, 68.35; H, 4.88. Found: C, 68.49; H, 4.93.

2-(3-Nitro-1-azulyl)ethyl Acetate (3-NO_2-1-OAc). To a solution of 44 mg (0.20 mmol) of 1-OAc in 2 ml of pyridine was added 0.5 ml of 0.6 M tetranitromethane in absolute ethanol and the mixture was allowed to stir at room temperature for 15 min. A mixture of 20 ml of ice-cold water and 25 ml of $CHCl_3$ was added to the red-brown solution. The layers were separated and the aqueous layer was extracted twice more with $CHCl_3$. The combined organic layers were washed with three 30-ml portions of 5% hydrochloric acid and 100 ml of water, and dried ($MgSO_4$). The solvent volume was reduced and the residue was chromatographed on alumina[28] where CH_2Cl_2 eluted 47 mg (89%) of 3-NO_2-1-OAc which was recrystallized several times from ethyl acetate, mp 98.6–99.0 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05. Found: C, 64.61; H, 4.82.

2-(3-Nitro-1-azulyl)ethanol (3-NO_2-1-OH). 1-OH (97 mg, 0.43 mmol) was nitrated with tetranitromethane as above in the preparation of 3-NO_2-1-OAc. It was chromatographed on alumina[28] where chloroform eluted 0.112 g (92%) of 3-NO_2-1-OH as a red oil which crystallized on standing, mp 105.0–106.0 °C. (See paragraph at end of paper regarding supplementary material.)

An α-naphthyl urethane was prepared in pyridine. It was chromatographed on alumina[28] where CH_2Cl_2 eluted it as an orange band. Repeated recrystallizations from 1:1 CCl_4–CH_2Cl_2 gave orange-red crystals, mp 184.2–184.5 °C.

Anal. Calcd for $C_{23}H_{18}N_2O_4$: C, 71.48; H, 4.69. Found: C, 71.21; H, 4.66.

2-(3-Nitro-1-azulyl)ethyl Tosylate (3-NO_2-1-OTs). A solution of 108 mg (0.50 mmol) of 3-NO_2-1-OH in 2.0 ml of dry pyridine was cooled to 0 °C. To this solution was added 150 mg (0.79 mmol) of toluenesulfonyl chloride and the mixture was allowed to stir at 0 °C for 3 h. A mixture of 20 ml of ice-cold water and 20 ml of $CHCl_3$ was added and the layers were separated. The aqueous layer was extracted with two 20-ml portions of $CHCl_3$ to remove the remaining orange color. The combined organic layers were washed with three 50-ml portions of ice-cold, 5% hydrochloric acid and once with 50 ml of cold water, and dried ($MgSO_4$). The solvent volume was reduced and the residue chromatographed on alumina[28] where CH_2Cl_2 eluted 170 mg (92%) of 3-NO_2-1-OTs which was subsequently recrystallized from hexane–CH_2Cl_2 to afford red plates, mp 124.4–124.9 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{19}H_{17}NO_5S$: C, 61.43; H, 4.61. Found: C, 61.14; H, 4.56.

Dimethyl 2-Methoxy-1,3-azulenedicarboxylate.[12a] To 150 ml of dry methanol [distilled from $Mg(OCH_3)_2$] was added 575 mg (25.0 mg-atoms) of sodium. When the sodium had dissolved, 1.58 g (5.15 mmol) of diethyl 2-chloro-1,3-azulenedicarboxylate[1a] in 100 ml of dry methanol was added. This mixture was heated under reflux with stirring for 2.5 h, the solvent volume reduced, and the residue chromatographed on alumina.[28] Benzene eluted a single, red band that afforded 1.330 g (94%) of the title compound. Recrystallization from methanol yielded needles, mp 64.5–65.5 °C (lit.[12a] mp 60–62 °C). (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{15}H_{14}O_5$: C, 65.69; H, 5.14. Found: C, 65.90; H, 5.14.

2-Methoxyazulene.[12a] To 500 mg (1.83 mmol) of dimethyl 2-methoxy-1,3-azulenedicarboxylate in 5 ml of ethanol was added 1.00 g (17.9 mmol) of potassium hydroxide in 10 ml of water. This mixture was heated under reflux with stirring for 2 h as the color changed from orange to red, transferred to a centrifuge tube, and acidified with 6 M hydrochloric acid. The resultant solid was collected, transferred with acetone into a large sublimation tube, and dried overnight at room temperature with an air stream.

This sample was heated to 200 °C (100 Torr) and a rose-violet sublimate formed on the condenser. The sublimate was removed with hexane and chromatographed on alumina.[28] Hexane developed a rose-colored band that was eluted with benzene to afford 230 mg (80%) of the title compound. Crystallization from methanol yielded red-violet crystals, mp 79.0–80.0 °C (lit.[12a] mp 82–83 °C). (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.60; H, 6.06.

2-(2-Methoxy-1-azulyl)ethyl Acetate (2-CH_3O-1-OAc). To 290 mg (1.83 mmol) of 2-methoxyazulene in 20 ml of CH_2Cl_2 with stirring at 0 °C was added 505 mg (3.80 mmol) of $AlCl_3$. An immediate change from a rose-red to a deep-red color occurred. After stirring for 5 min 8 ml of a 2% solution (v/v) of ethylene oxide was added and a red-brown coloration was observed. The mixture was stirred for an additional 20 min, diluted with 100 ml of ice-cold water, and extracted with three 50-ml portions of CH_2Cl_2. The combined extracts were washed with eight 75-ml portions of 10% hydrochloric acid and dried (Na_2SO_4), the solvent volume reduced, and the residue chromatographed on alumina[28] with CH_2Cl_2 which eluted a red band that afforded 178 mg of unreacted 2-methoxyazulene. $CHCl_3$ eluted a violet band that yielded 130 mg (35%, 92% net) of crude 2-CH_3O-1-OH.

2-CH_3-1-OH was acetylated with acetic anhydride in pyridine at 0 °C. After normal work-up, the acetate was chromatographed on alumina[28] with 4:1 C_6H_6–CH_2Cl_2. A violet band eluted and was rechromatographed giving the acetate in 60% overall yield which crystallized from hexane as fine, violet needles, mp 25.0–27.0 °C. (See paragraph at end of paper regarding supplementary material.)

For analysis a TNB complex was prepared and crystallized from 1:1 ethyl acetate–hexane to afford red-brown needles, mp 106.0–106.5 °C.

Anal. Calcd for $C_{21}H_{19}O_9N_3$: C, 55.14; H, 4.19. Found: C, 54.95; H, 4.30.

2-(2-Methoxy-1-azulyl)ethanol (2-CH_3O-1-OH). To 123 mg (0.50 mmol) of 2-CH_3O-1-OAc dissolved in 4 ml of ethanol and 0.5 ml of water was added 300 mg (5.4 mmol) of potassium hydroxide. This mixture was stirred at 0 °C for 2 h, diluted with 100 ml of ice-cold water, and extracted with three 50-ml portions of ether. The combined ether layers were washed once with 100 ml of water and dried (Na_2SO_4), and the solvent volume was reduced. The residue was chromatographed on alumina[28] where $CHCl_3$ eluted a single, violet-red band that afforded 95 mg (94%) of a violet oil. (See paragraph at end of paper regarding supplementary material.)

For analysis a TNB complex was prepared and crystallized from 1:1 ethyl acetate–hexane to afford red plates: mp 131.0–132.0 °C; λ_{max} (CH_2Cl_2) 283 nm (log ϵ 4.72), 293 (4.81), 318 (3.89), 345 (3.61), 361 (3.69), 375 (3.51), 535 (2.35), 570 (2.14), and 625 (1.69).

Anal. Calcd for $C_{19}H_{17}O_8N_3$: C, 54.94; H, 4.13. Found: C, 54.95; H, 4.15.

2-(2-Methoxy-1-azulyl)ethyl Tosylate (2-CH_3O-1-OTs). 2-CH_3O-1-OH (95 mg, 0.47 mmol) was converted to its tosylate ester by the method given for 1-OTs. It was chromatographed on deactivated (4.5% H_2O) alumina[28] where CH_2Cl_2 eluted it as a violet band yielding 140 mg (84%) of 2-CH_3O-1-OTs as a violet oil which crystallized on standing.

This unstable solid was converted to a TNB complex which crystallized as red-brown microcrystals, mp 96.5–97.5 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{26}H_{23}O_{10}N_3S$: C, 54.83; H, 4.07; N, 7.38. Found: C, 55.15; H, 3.99; N, 7.55.

2-Methylazulene. This was prepared by the method of Nozoe et al.[12a] using the thermal decarboxylation procedure as given above in the synthesis of 2-methoxyazulene, 260 °C (100 Torr). After chromatography, a 42% yield of 2-methylazulene was obtained, violet crystals, mp 48–49 °C (lit.[12a] mp 49–50 °C). (See paragraph at end of paper regarding supplementary material.)

For analysis a TNB complex was prepared and crystallized from 1:1 hexane–ethyl acetate, mp 42.5–43.5 °C.

Anal. Calcd for $C_{17}H_{13}O_6N_3$: C, 57.49; H, 3.69; N, 11.83. Found: C, 57.60; H, 4.03; N, 11.60.

2-(2-Methyl-1-azulyl)ethanol (2-CH_3-1-OH). Following the direct β-hydroxyethylation procedure described for the synthesis of 2-CH_3O-1-OAc, 124 mg (0.88 mmol) of 2-methylazulene and 70 mg of $AlCl_3$ in 30 ml of CH_2Cl_2 at 0 °C was treated with 5 ml of a 2% solution of ethylene oxide in CH_2Cl_2. After work-up the residue was chromatographed on alumina.[28] CH_2Cl_2 eluted a violet band to afford 100 mg of unreacted 2-methylazulene. $CHCl_3$ eluted a blue band, and a second smaller blue band was removed with absolute ethanol. Rechromatography of the first blue band afforded 25 mg (15%, 75% net) of 2-CH_3-1-OH as a blue band. (See paragraph at end of paper regarding supplementary material.)

A TNB complex was prepared for analysis and crystallized from 1:1 ethyl acetate–hexane to afford red-brown crystals: mp 144.0–144.5 °C; λ_{max} (CH_2Cl_2) 281 nm (log ε 4.68), 289 (4.76), 304 (3.74), 334 (3.50), 349 (3.61), 576 (2.36), 615 (2.30), and 687 (1.83).

Anal. Calcd for $C_{19}H_{17}O_7N_3$: C, 57.14; H, 4.29. Found: C, 57.20; H, 4.10.

The second, smaller, blue band afforded 10 mg (5%, 25% net) of 1,3-bis(2-hydroxyethyl)-2-methylazulene: NMR ($CDCl_3$, internal Me_4Si) τ 1.82 [d (J = 8.5 Hz), $C_{4,8}$ H's, 2], 2.57–2.84 (m, C_6 H, 1), 3.00 [t (J = 8.5 Hz), $C_{5,7}$ H's, 2], 6.25 (t (J = 6 Hz), α-CH_2, 4], 6.75 [t (J = 6 Hz), β-CH_2, 4], 7.47 (s, CH_3, 3), and 7.92 (s, OH, 2).

A TNB complex was prepared for analysis and crystallized from 1:1 ethyl acetate–hexane to afford red-brown crystals: mp 122–123 °C; ir (KBr) 3.00 (s, O–H) and 9.60 μ (s, C–O); λ_{max} (CH_2Cl_2) 287 nm (log ε 4.70), 294 (4.75), 307 (3.90), 338 (3.54), 353 (3.68), 369 (3.12), 595 (2.40), 635 (2.34), and 710 (1.90).

Anal. Calcd for $C_{21}H_{21}O_8N_3$: C, 56.88; H, 4.77. Found: C, 56.53; H, 4.94.

2-(2-Methyl-1-azulyl)ethyl Tosylate (2-CH_3-1-OTs). The tosylate ester of 2-CH_3-1-OH (95 mg, 0.51 mmol) was prepared in the usual way described for 1-OTs. After work-up, the ester was chromatographed on deactivated (3% H_2O) alumina[28] where CH_2Cl_2 eluted two blue bands. After solvent removal, the second band gave 38 mg of unreacted 2-CH_3-1-OH, and the first band yielded 83 mg (48%, 80% net) of unstable, blue 2-CH_3-1-OTs.

This unstable tosylate was dissolved in 0.8 ml of ethyl acetate to which had been added 57 mg (0.268 mmol) of TNB. An equal volume of hexane was added and the solution cooled to afford red-brown rosettes, mp 92.5–93.0 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{26}H_{23}O_9N_3S$: C, 56.41; H, 4.19. Found: C, 56.60; H, 4.21.

2-(2-Chloro-1-azulyl)ethanol (2-Cl-1-OH). Following the direct β-hydroxyethylation procedure described for the synthesis of 2-CH_3O-1-OAc, 255 mg (1.57 mmol) of 2-chloroazulene[12a] and 420 mg of $AlCl_3$ in 25 ml of CH_2Cl_2 at 0 °C were treated with 8 ml of a 2% solution of ethylene oxide in CH_2Cl_2. After work-up the residue was chromatographed on alumina.[28] Hexane eluted a violet band followed closely by a blue band. $CHCl_3$ developed and eluted a second blue band, and absolute ethanol removed a third blue band of unstable material that decomposed upon solvent evaporation.

The violet band afforded 150 mg of unreacted 2-chloroazulene. The first blue band yielded 5 mg (1%, 2% net) of bis(2-chloro-1-azulyl)methane which crystallized from 1:1 CCl_4–hexane to give blue, fluffy crystals: mp 193–194 °C; NMR (CCl_4, internal Me_4Si) τ 1.54–2.00 (m, 4), 2.44–3.17 (m, 8) and 5.14 (s, CH_2, 2); λ_{max} (cyclohexane) 279 nm (log ε 4.90), 292 (4.85), 335 (3.88), 351 (4.02), 364 (3.44), 573 (2.78), 615 (2.73), 670 (2.33), and 685 (2.28).

Anal. Calcd for $C_{21}H_{14}Cl_2$: C, 74.79; H, 4.18. Found: C, 75.10; H, 4.22.

The second blue band afforded 75 mg (23%, 57% net) of solid 2-Cl-1-OH: mp 32–33 °C; NMR ($CDCl_3$, internal Me_4Si) τ 1.57–2.04 (m, $C_{4,8}$ H's, 2), 2.24–3.14 (m, $C_{3,5,6,7}$ H's, 4), 6.19 [t (J = 6 Hz), α-CH_2, 2], 6.72 [t (J = 6 Hz), β-CH_2, 2], and 8.02 (s, OH, 1). For analysis a TNB complex was prepared and crystallized from 1:1 ethyl acetate–hexane to give red-brown needles: mp 95.5–96.0 °C; ir (KBr) 3.04 (m, OH) and 9.60 μ (m, C–O); λ_{max} (CH_2Cl_2) 283 nm (log ε 4.85), 291 (4.86), 304 (3.90), 324 (3.55), 334 (3.72), 348 (3.81), 565 (2.56), 600 (2.52), and 660 (2.11).

Anal. Calcd for $C_{18}H_{14}O_7N_3Cl$: C, 51.50; H, 3.36. Found: C, 51.80; H, 3.76.

2-(2-Chloro-1-azulyl)ethyl Tosylate (2-Cl-1-OTs). The tosylate ester of 2-Cl-1-OH (85 mg, 0.41 mmol) was prepared in the usual way described for 1-OTs. After work-up the ester was chromatographed on deactivated (7.4% H_2O) alumina[28] with CH_2Cl_2. The solvent was removed from the single, violet band to yield 138 mg (93%) of 2-Cl-1-OTs as a violet oil: NMR ($CDCl_3$, internal Me_4Si) τ 1.78–2.93 (m, 10), 5.73 [t (J = 7 Hz), α-CH_2, 2], 6.63 [t (J = 7 Hz), β-CH_2, 2], and 7.68 (s, tosyl CH_3, 3).

The tosylate was converted to its TNB complex. Four recrystallizations gave red-brown crystals: mp 110.0–111.5 °C; ir (KBr) 8.40 (w, S–O) and 8.50 μ (s, S–O); λ_{max} (CH_2Cl_2) 660 nm (log ε 2.09), 600 (2.51), 561 (2.55), 347 (3.76), 333 (3.64), 291 (4.79), and 282 (4.78).

Anal. Calcd for $C_{25}H_{20}O_9N_3SCl$: C, 52.32; H, 3.51. Found: C, 52.62; H, 3.44.

Diethyl 2-Bromo-1,3-azulenedicarboxylate. To 304 mg (1.06 mmol) of diethyl 2-amino-1,3-azulenedicarboxylate[1a] in 60 ml of dioxane with ice cooling and stirring was added 0.3 ml of concentrated H_2SO_4 and 250 mg (3.63 mmol) of $NaNO_2$ dissolved in 0.5 ml of water and 5 ml of dioxane. After 3–5 min the color changed from orange to green, and 0.4 ml of concentrated H_2SO_4 and 2.0 g (19.3 mmol) of NaBr in 2 ml of water were added. After an additional 5–10 min, a blue oil separated from the green solution and was visible on the flask walls. Three 250-ml portions of anhydrous ether were successively added and decanted from the mixture to precipitate and wash the diazonium salt. To this blue salt was added 100 ml of dry THF. Nitrogen evolution and a color change from blue to red was immediately observed. The mixture was allowed to stir for 30 min under cooling and filtered, the solvent volume reduced, and the residue chromatographed on alumina.[28] Benzene eluted a red band that afforded 245 mg (66%) of the title compound. Crystallization from ethanol yielded red crystals, mp 78.0–78.5 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{16}H_{15}O_4Br$: C, 54.72; H, 4.31. Found: C, 54.80; H, 4.29.

2-Bromoazulene. A solution of 240 mg (0.684 mmol) of diethyl 2-bromo-1,3-azulenedicarboxylate in 1.6 ml of ethanol and 210 mg (3.75 mmol) of potassium hydroxide in 0.4 ml of water was heated under reflux for 30 min with stirring, cooled, transferred to a centrifuge tube, acidified with 10% hydrochloric acid, washed with six 25-ml portions of water, and dried under an air stream to yield 179 mg of crude diacid.

This sample was placed in a large sublimation tube and heated to 240 °C (200 Torr). The violet sublimate that collected on the condenser was removed with hexane and chromatographed on alumina.[28] Hexane eluted a violet band that afforded 110 mg (78%) of 2-bromoazulene. Crystallization from hexane yielded violet plates: mp 104.2–104.8 °C; ir (CCl_4) no characteristic absorptions; NMR (CCl_4, internal Me_4Si) τ 1.70–1.98 (m, $C_{4,8}$ H's, 2) and 2.40–3.10 (m, 5); λ_{max} (cyclohexane) 281 nm (log ε 4.81), 289 (4.88), 303 (3.86), 332 (3.78), 346 (3.86), 359 (3.74), 557 (2.70), 596 (2.66), and 655 (2.25).

2-(2-Bromo-1-azulyl)ethyl Acetate (2-Br-1-OAc). Following the direct β-hydroxyethylation procedure described for the synthesis of 2-CH_3O-1-OAc, 400 mg (1.93 mmol) of 2-bromoazulene and 550 mg of $AlCl_3$ in 30 ml of CH_2Cl_2 at 0 °C was treated with 9.2 ml of a 2% solution of ethylene oxide in CH_2Cl_2. After 1 h, work-up gave a residue which was chromatographed on alumina[28] where CCl_4 eluted a broad, violet band of unreacted 2-bromoazulene (230 mg) followed by a blue band. Continued elution with $CHCl_3$ yielded a second blue band which afforded 175 mg (36%, 85% net) of crude 2-Br-1-OH. Absolute ethanol eluted a third blue band of unstable material that decomposed immediately after solvent removal.

The first blue band afforded 25 mg (3%, 7% net) of material identified as bis(2-bromo-1-azulyl)methane which crystallized from 1:1 $CHCl_3$–hexane as blue needles, mp 185.0–190.0 °C dec. (See paragraph at end of paper regarding supplementary material.)

The 175 mg of crude 2-Br-1-OH was acetylated with acetic anhydride in pyridine at 0°. Work-up and chromatography on alumina[28] with CH_2Cl_2 eluted a single, blue band. Solvent volume reduction and rechromatography with 3:1 CCl_4–CH_2Cl_2 afforded 165 mg

(81%) of 2-Br-1-OAc as a blue oil. (See paragraph at end of paper regarding supplementary material.)

For analysis a TNB complex was prepared and crystallized from 1:1 ethyl acetate–hexane to afford red-brown plates: mp 79.5–80.0 °C; λ_{max} (CH_2Cl_2) 285 nm (log ϵ 4.81), 295 (4.82), 334 (3.69), 349 (3.78), 361 (3.17), 566 (2.59), 605 (2.55), and 660 (2.21).

Anal. Calcd for $C_{20}H_{16}O_8N_3Br$: C, 47.45; H, 3.19. Found: C, 47.63, H, 3.33.

2-(2-Bromo-1-azulyl)ethanol (2-Br-1-OH). Basic hydrolysis of 240 mg (0.47 mmol) of 2-Br-1-OAc·TNB complex was carried out as in the synthesis of 2-CH_3O-1-OH from its acetate. After work-up, the residue was chromatographed on alumina[28] where CH_2Cl_2 developed and $CHCl_3$ eluted a blue band that yielded 108 mg (92%) of 2-Br-1-OH. (See paragraph at end of paper regarding supplementary material.)

A TNB complex was prepared and crystallized for analysis from 1:1 ethyl acetate–hexane to yield red-brown needles: mp 105.0–105.5 °C; λ_{max} (CH_2Cl_2) 285 nm (log ϵ 4.79), 295 (4.80), 335 (3.69), 349 (3.76), 362 (3.13), 568 (2.58), 605 (2.53), and 665 (2.14).

Anal. Calcd for $C_{18}H_{14}O_7N_3Br$: C, 46.57; H, 3.04. Found: C, 46.81; H, 3.27.

2-(2-Bromo-1-azulyl)ethyl Tosylate (2-Br-1-OTs). 2-Br-1-OH (105 mg, 0.43 mmol) was converted to its tosylate ester by the standard method used for 1-OTs. After work-up, the tosylate was chromatographed on deactivated (4.6% H_2O) alumina.[28] CH_2Cl_2 eluted a violet band that afforded 138 mg (81%) of 2-Br-1-OTs as a blue oil: ir (neat film) 8.35 (s, S–O) and 8.45 μ (s, S–O).

A TNB complex was produced as long, dense, dark-red needles: mp 114.0–114.5 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{25}H_{20}O_9N_3BrS$: C, 48.55; H, 3.26. Found: C, 48.67; H, 3.32.

2-(2-Iodo-1-azulyl)ethyl Acetate (2-I-1-OAc). Following the direct β-hydroxyethylation procedure described for the synthesis of 2-CH_3O-1-OAc, 475 mg (1.87 mmol) of 2-iodoazulene[12a] and 545 mg of $AlCl_3$ in 25 ml of CH_2Cl_2 at 0 °C was treated with 9.2 ml of a 2% solution of ethylene oxide in CH_2Cl_2. After 35 min, work-up gave a residue which was chromatographed on alumina.[28] CH_2Cl_2 eluted a broad, blue band that afforded 285 mg of unreacted 2-iodoazulene, and $CHCl_3$ eluted a blue band that yielded 205 mg of crude 2-I-1-OH. Absolute ethanol eluted a third, blue band that yielded 20 mg of material which was not investigated.

The 2-I-1-OH was acetylated with acetic anhydride and pyridine at 0 °C. After work-up the residue was chromatographed on alumina.[28] CCl_4–CH_2Cl_2 (1:1) eluted a broad, blue band, CH_2Cl_2 removed a diffuse, blue band, and $CHCl_3$ eluted a narrow, blue band. Only the first blue band was investigated and afforded 160 mg (25%, 63% net) of 2-I-1-OAc. Crystallization from hexane afforded blue rosettes, mp 69.0–69.5 °C. (See paragraph at end regarding supplementary material.)

Anal. Calcd for $C_{14}H_{13}O_2I$: C, 49.43; H, 3.85. Found: C, 49.56; H, 3.90.

2-(2-Cyano-1-azulyl)ethyl Acetate (2-CN-1-OAc). A mixture of 137 mg (0.40 mmol) of 2-I-1-OAc and 53 mg (0.60 mmol) of CuCN in 10 ml of dry DMF was heated at 150 °C with stirring for 2 h. The color of this mixture changed during this period from blue to blue-brown. The mixture was cooled, diluted with 100 ml of benzene, and washed with six 100-ml porions of warm, aqueous NaCN (prepared from 600 ml of warm water and 20 g of NaCN). The organic layer was washed with water and dried (Na_2SO_4), the solvent volume reduced, and the residue chromatographed on alumina.[28] CCl_4–CH_2Cl_2 (1:1) eluted a violet band, CH_2Cl_2 eluted a broad, blue band, anhydrous ether eluted a blue-green band, and $CHCl_3$ eluted a violet and a green-blue band. The broad, blue band afforded 83 mg (86%) of 2-CN-1-OAc. The other bands were not investigated. The product acetate was isolated as a blue-green oil. (See paragraph at end of paper regarding supplementary material.)

For analysis a TNB complex was prepared and crystallized from 1:1 ethyl acetate–hexane. Recrystallization yielded green spherulites: mp 96.6–97.5 °C; λ_{max} (CH_2Cl_2) 256 nm (log ϵ 4.47) (sh), 289 (4.69), 300 (4.64), 334 (3.78), 342 (3.75), 347 (3.81), 357 (3.48), 606 (2.69), 648 (2.70), and 710 (2.45) (sh).

Anal. Calcd for $C_{21}H_{16}O_8N_4$: C, 55.75; H, 3.57. Found: C, 55.98; H, 3.73.

2-(2-Cyano-1-azulyl)ethanol (2-CN-1-OH). Basic hydrolysis of 210 mg (0.88 mmol) of 2-CN-1-OAc was carried out as in the synthesis of 2-CH_3O-1-OH from its acetate. After work-up the residue was chromatographed on alumina[28] where $CHCl_3$ eluted a single, blue band that yielded 170 mg (99%) of the title compound. Crystallization from 1:1 ether–hexanes afforded green needles, mp 50.0–50.5 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{13}H_{11}ON$: C, 79.16; H, 5.62. Found: C, 79.29; H, 5.64.

2-(2-Cyano-1-azulyl)ethyl Tosylate (2-CN-1-OTs). 2-CN-1-OH (140 mg, 0.71 mmol) was converted to its tosylate ester by the standard method used for 1-OTs. After work-up, the tosylate was chromatographed on deactivated (4.6% H_2O) alumina with CH_2Cl_2. A blue band was eluted which afforded 235 mg (94%) of the title compound which was crystallized from CH_2Cl_2 and hexane as long, dense, green needles, mp 109.2–110.0 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{20}H_{17}O_3SN$: C, 68.35; H, 4.88. Found: C, 68.46; H, 4.96.

Diethyl 6-Bromo-1,3-azulenedicarboxylate (7). To a 2.00 g (5.46 mmol) of diethyl 2-amino-6-bromo-1,3-azulenedicarboxylate (**6**)[12a] in 350 ml of dioxane was added 535 mg of concentrated sulfuric acid in 10 ml of tetrahydrofuran and 600 mg (5.45 mmol) of *p*-hydroquinone. In two addition funnels were placed separately 11.20 g (102 mmol) of *p*-hydroquinone in 200 ml of dioxane and 12.5 g (107 mmol) of isoamyl nitrite in 200 ml of dioxane. The contents of the two addition funnels were added simultaneously at approximately equal rates at room temperature to the stirred solution as the color changed from orange to red. This mixture was stirred for 3 h, diluted with 500 ml of 1 M aqueous sodium sulfite, and extracted with three 500-ml portions of hexane. The combined extracts were washed with two 500-ml portions of water and dried (Na_2SO_4), and the solvent volume reduced. The residue was chromatographed on alumina.[28] Benzene eluted a red band and developed a yellow band that was eluted with CH_2Cl_2. The yellow band afforded 80 mg of unreacted **6** and the red band gave 1.791 g (93%, 97% net) of **7**. Crystallization from benzene yielded dark, red needles, mp 206.0–207.5 °C (lit.[12a] 26%, mp 206–207 °C). (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{16}H_{15}O_4Br$: C, 54.72; H, 4.31. Found: C, 54.70; H, 4.53.

Dimethyl 6-Methoxy-1,3-azulenedicarboxylate (12). To 125 ml of methanol [distilled from $Mg(OCH_3)_2$] was added 253 mg (11.0 mg-atoms) of sodium. After the sodium had dissolved, 1.00 g (2.73 mmol) of **7** was added with stirring and the solution was heated under reflux for 3 h with a gradual color change from red to orange. The methanol was removed on a rotary evaporator and the residue was chromatographed on alumina.[28] Benzene developed a small red band in front of the large orange band and the red band was collected to yield 40 mg of **7** by analysis of the NMR spectrum. The major portion of the orange band was eluted with CH_2Cl_2 to give 640 mg (82%, 85.5% net) of **12**. Crystallization of this product from benzene gave orange needles, mp 149–150.2 °C. (See paragraph at end of paper regarding supplementary material.)

6-Methoxyazulene (17). When 640 mg (2.34 mmol) of **12** was dissolved in 80 ml of concentrated H_2SO_4, a yellow solution resulted. After stirring for 2 h at 25 °C, no color change was noted. This solution was poured slowly into 800 ml of ice water with stirring with the immediate formation of an orange-yellow precipitate. This solid was collected by centrifugation and washed with eight 30-ml portions of water. After drying (12 h, 50 °C), 555 mg (96.5%) of 6-methoxy-1,3-azulenedicarboxylic acid was obtained: NMR (Me_2SO-d_6, internal Me_4Si) τ −2.30 (broad s, CO_2H, 2), 0.36 [d (J = 11.5 Hz), $C_{4,8}$ H's, 2], 1.62 (s, C_2 H, 1), 2.44 [d (J = 11.5 Hz), $C_{5,7}$ H's, 2], and 5.92 (s, OCH_3, 3).

This sample was placed in a large sublimation tube and heated to 240–250 °C (160 Torr) for 8 h. During this time, violet plates formed on the condenser and were removed periodically. This product was chromatographed on alumina with 9:1 hexane–CH_2Cl_2 to yield, after solvent evaporation, 247 mg (67% based on starting diester) of **17**: mp 113–113.5 °C (lit.[30] 112–113 °C); ir (KBr) 6.30 (m), 9.90 (m), 12.07 (s), and 13.39 μ (s); NMR (CCl_4, internal Me_4Si) τ 1.91 [d (J = 10.5 Hz), $C_{4,8}$ H's, 2], 2.46 [t (J = 4.0 Hz), C_2 H, 1], 2.83 [d (J = 4.0 Hz), $C_{1,3}$ H's, 2], 3.34 [d(J = 10.5 Hz), $C_{5,7}$ H's, 2], and 6.13 (s, OCH_3, 3); λ_{max} (cyclohexane) 635 nm (log ϵ 1.80), 605 (1.93), 579 (3.34), 551 (2.29), 533 (2.34), 514 (2.28), 366 (3.48), 353 (3.67), 344 (3.59), 338 (3.58), 330 (3.51), 310 (3.93), 293 (4.82), 287 (4.80), and 282 (4.77).

Anal. Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.70; H, 6.51.

2-(6-Methoxy-1-azulyl)ethyl Tosylate (6-CH_3O-1-OTs). 6-CH_3O-1-OH[5] (135 mg, 0.67 mmol) was converted to its tosylate

ester under the conditions used for 1-OTs. Work-up and chromatography on deactivated (4% H_2O) alumina[28] with CH_2Cl_2 gave 238 mg (80%) of 6-CH_3O-1-OTs as an unstable violet-red oil: ir (neat film) 6.32 (s), 8.34 (s, S–O), and 8.47 μ (s, S–O); NMR ($CDCl_3$, internal Me_4Si) τ 1.80–3.40 (m, 10), 5.71 [t (J = 7.0 Hz), α-CH_2, 2], 6.12 (s, OCH_3, 3), 6.65 [t (J = 7.0 Hz), β-CH_2, 2], and 7.65 (s, CH_3, 3).

The product was converted to the TNB complex, which would not crystallize from ethyl acetate–hexane. However, upon standing at freezer temperature (−27 °C) for 1 week, a brown solid resulted, which softened at room temperature to a semisolid. Repeated attempts to purify this sample by recrystallization or chromatography did not yield a crystalline compound, but gave a solid with each cooling at freezer temperature which partially melted at room temperature. This complex was unstable at room temperature in the presence of air or in CH_2Cl_2 solution at room temperature over a 2-day period: λ_{max} (CH_2Cl_2) 539 nm (log ϵ 2.40), 370 (3.21), 357 (3.70), 350 (3.62), 342 (3.59), 297 (4.76), and 291 (4.76).

2-(6-Methyl-1-azulyl)ethyl Tosylate (6-CH_3-1-OTs). 6-CH_3-1-OH[5] (115 mg, 0.62 mmol) was converted to its tosylate ester by the method used for 1-OTs. Work-up and chromatography on deactivated (6% H_2O) alumina[28] with CH_2Cl_2 eluted two blue bands. After solvent removal, the first, blue band afforded 174 mg (83%) of 6-CH_3-1-OTs and the second band gave 20 mg of unreacted 6-CH_3-1-OH.

The tosylate ester was converted to its TNB complex as clusters of red-brown needles, mp 99.0–99.5 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{26}H_{23}N_3O_9S$: C, 56.41; H, 4.18. Found: C, 56.80; H, 4.02.

2-(6-Methyl-1-azulyl)ethyl Acetate (6-CH_3-1-OAc). 6-CH_3-1-OH (74 mg, 0.40 mmol) was acetylated with acetic anhydride in pyridine at 0 °C. Work-up and chromatography on alumina[28] gave 63 mg (75%) of the acetate (CH_2Cl_2 eluent) as a blue oil. This was converted to its TNB complex as long, violet-brown needles from ethyl acetate–hexane, mp 104.8–105.1 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{21}H_{19}N_3O_8$: C, 57.14; H, 4.34. Found: C, 57.37; H, 5.23.

6-Bromoazulene (16). Diethyl 6-bromo-1,3-azulenedicarboxylate (**7**, 500 mg, 1.42 mmol) was dissolved in 20 ml of concentrated H_2SO_4 and the resultant yellow solution stirred for 2 h at room temperature. This solution was poured into 200 ml of ice water with an instantaneous formation of a finely divided red solid. The precipitate was collected by centrifugation and the gelatinous precipitate washed with ten 15-ml portions of water. The product was collected and dried (70 °C, 4 h) to yield 402 mg (96%) of 6-bromo-1,3-azulenedicarboxylic acid, which was finely ground and placed in a large sublimation tube. Upon heating to 230 °C (200 Torr) a blue solid appeared on the condenser. Heating was maintained for 10 h with periodic removal of the product from the condenser. Chromatography of this compound on alumina[28] with 9:1 hexane–CH_2Cl_2 yielded 133 mg (47%, 45% based on starting ester) of **16**: mp 106.5–108.0 °C; ir (KBr) 10.49 (m), 12.11 (s), and 13.28 μ (m); NMR (CCl_4, internal Me_4Si) τ 1.92–2.21 (m, 3) and 2.46–2.70 (m, 4); λ_{max} (cyclohexane) 702 nm (log ϵ 2.13), 662 (2.14), 636 (2.46), 607 (2.45), 582 (2.49), 560 (2.41), 539 (2.32), 521 (2.17), 362 (3.13), 347 (3.77), 340 (3.58), 334 (3.63), 304 (3.80), 288 (4.90), 282 (4.85), and 278 (4.81). A sublimed sample, mp 104.5–105.0°, was submitted for analysis.

Anal. Calcd for $C_{10}H_7Br$: C, 57.99; H, 3.41. Found: C, 58.10; H, 3.65.

2-(6-Bromo-1-azulyl)ethyl Tosylate (6-Br-1-OTs). 6-Br-1-OH[5] (24 mg, 0.096 mmol) was converted to its tosylate ester under the conditions outlined for 1-OTs. Isolation and purification of the product gave 32 mg (82%) of 6-Br-1-OTs as silky blue needles, mp 92.2–93.0 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{19}H_{17}O_3SBr$: C, 56.31; H, 4.23. Found: C, 56.37; H, 4.36.

2-(6-Cyano-1-azulyl)ethyl Acetate (6-CN-1-OAc). 6-Br-1-OAc (180 mg, 0.62 mmol) (produced by Ac_2O–pyridine acetylation of 6-Br-1-OH) and 83 mg (0.93 mmol) of CuCN in 10 ml of dry DMF was heated for 6.5 h at 135 °C with stirring under an N_2 atmosphere. Work-up (see synthesis of 2-CN-1-OAc) and chromatography on alumina[28] with CH_2Cl_2 first eluted 30 mg of unreacted 6-Br-1-OAc. This was followed by a blue band containing 100 mg (68%) of 6-CN-1-OAc as a green oil: ir (neat film) 4.52 (m, C≡N), 5.75 (s, C=O), and 9.60 μ (s, C–O); NMR (CCl_4, internal Me_4Si) τ 1.73–2.97 (m, 6), 5.73 [t (J = 7 Hz), α-CH_2, 2], 6.68 [t (J = 7 Hz), β-CH_2, 2], and 8.03 (s, CH_3, 3).

For analysis a TNB complex was prepared and crystallized from 1:1 ethyl acetate–hexane to yield green plates: mp 80.0–80.5 °C; λ_{max} (CH_2Cl_2) 280 nm (log ϵ 4.88) (sh), 290 (5.07), 306 (3.95) (sh), 337 (3.80), 354 (3.88), 654 (2.53), and 722 (2.46).

Anal. Calcd for $C_{21}H_{16}O_8N_4$: C, 55.75; H, 3.57. Found: 55.72; H, 3.53.

2-(6-Cyano-1-azulyl)ethanol (6-CN-1-OH). Basic hydrolysis of 110 mg (0.46 mmol) of 6-CN-1-OAc was carried out as in the synthesis of 2-CH_3O-1-OH from its acetate. After work-up, the green residue was chromatographed on alumina[28] where $CHCl_3$ eluted a single, light-blue band that yielded 90 mg (100%) of 6-CN-1-OH as a green oil: ir (neat film) 3.00 (s, OH), 4.55 (s, CN), and 9.60 μ (s, C–O); NMR ($CDCl_3$, internal Me_4Si) τ 1.73–2.97 (m, 6), 6.12 [t (J = 6 Hz), α-CH_2, 2], 6.75 [t (J = 6 Hz), β-CH_2, 2], and 7.42 (s, OH, 1).

For analysis a TNB complex was prepared and crystallized from 1:1 ethyl acetate–hexane to give light-brown needles: mp 77–78 °C; λ_{max} (CH_2Cl_2) 281 nm (log ϵ 4.85) (sh), 290 (5.03), 338 (3.68), 353 (3.80), 657 (2.53), and 725 (2.44).

Anal. Calcd for $C_{19}H_{14}O_7N_4$: C, 55.61; H, 3.44. Found: C, 55.54; H, 3.28.

2-(6-Cyano-1-azulyl)ethyl Tosylate (6-CN-1-OTs). 6-CN-1-OH (90 mg, 0.46 mmol) was converted to its tosylate ester under conditions as in the synthesis of 1-OTs. Work-up gave a green residue which was chromatographed on deactivated (6% H_2O) alumina[28] where CH_2Cl_2 eluted two blue bands. The second band contained 10 mg of unreacted 6-CN-1-OH while the first band afforded 125 mg (78%) of 6-CN-1-OTs. The tosylate was crystallized from 1.5 ml of 1:1 ethyl acetate–hexane to afford green crystals, mp 118.0–119.5 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{20}H_{17}O_3NS$: C, 68.35; H, 4.88. Found: C, 68.26; H, 4.98.

6-Cyanoazulene. To 60 mg (0.29 mmol) of 6-bromoazulene was added 4 ml of dry DMF and 34 mg (0.38 mmol) of CuCN. The mixture was heated to 150 °C and maintained at this temperature for 6 h with stirring. The cooled mixture was diluted with 50 ml of benzene and the benzene layer was shaken vigorously with three portions of warm, concentrated aqueous NaCN solution. The organic layer was then washed with water and dried (Na_2SO_4), and the solvent volume reduced. The concentrated green benzene solution was chromatographed on alumina.[28] Benzene developed a blue band which was eluted with 1:1 hexane–CH_2Cl_2 to yield, after solvent removal, 35 mg (78%) of 6-cyanoazulene: mp 51–52 °C; ir (film) 4.52 (m, C≡N), 11.97 (s), 12.82 (s), and 13.21 μ (s); NMR (CCl_4, internal Me_4Si) τ 1.64 [d (J = 10.0 Hz), $C_{4,8}$ H's, 2], 1.90 [t (J = 4.0 Hz), C_2H, 1], 2.46 [d (J = 4.0 Hz), $C_{1,3}$ H's, 2], and 2.59 [d (J = 10.0 Hz), $C_{5,7}$ H's, 2]; λ_{max} (cyclohexane) 774 nm (log ϵ 1.96), 721 (2.20), 696 (2.54), 660 (2.51), 631 (2.57), 606 (2.48), 584 (2.40), 362 (3.70), 346 (3.82), 333 (3.65), and 283 (4.01).

Anal. Calcd for $C_{11}H_7N$: C, 86.24; H, 4.61. Found: C, 86.20; H, 4.81.

Diethyl 2-Nitroaminoazulene-1,3-dicarboxylate (21). Diethyl 2-amino-1,3-azulenedicarboxylate (**3**,[1a] 500 mg, 1.74 mmol) was dissolved in 15 ml of acetic anhydride and the orange solution was chilled in a dry ice–2-propanol bath. To the cold solution was added 521 mg (2.16 mmol) of $Cu(NO_3)_2$·$(H_2O)_3$ dissolved in 25 ml of acetic anhydride over a 10-min period with stirring, resulting in a green solution. The solution was allowed to warm to room temperature, the color changing to brown. The solution was diluted with cold water and extracted with CH_2Cl_2. The CH_2Cl_2 was extracted three times with dilute NH_4OH, imparting an orange-red color to the NH_4OH layer. The CH_2Cl_2 layer was washed with water and dried ($MgSO_4$), and the solvent evaporated. The residue was chromatographed on basic alumina with CH_2Cl_2 to yield, after evaporation of solvent, 224 mg of starting **3**.

The NH_4OH extracts were combined, neutralized with 5% hydrochloric acid, and extracted with CH_2Cl_2. The red organic layer was washed with water and dried ($MgSO_4$), and the solvent volume reduced to give 233 mg (40.3%, 73% net yield) of **21**. An analytical sample was prepared by recrystallization from a minimum amount of CH_2Cl_2 affording large, orange-red needles, mp 147–149 °C. (See paragraph at end of paper regarding supplementary material.)

Anal. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.86. Found: C, 57.71; H, 5.03.

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Registry No.—1-OH, 26157-06-2; 3-CH_3O-1-OH, 58311-89-0; 3-CH_3O-1-OH TNB complex, 58311-90-3; 3-CH_3-1-OH, 58311-91-4; 3-CH_3-1-OH TNB complex, 58311-92-5; 3-CH_3S-1-OH, 58311-93-6; 3-Br-1-OH, 58311-94-7; 3-CH_3CO-1-OH, 58311-95-8; 3-CN-1-OH, 58311-96-9; 3-CN-1-OH 2TNB complex, 58311-97-0; 3-NO_2-1-OH, 26157-07-3; 3-NO_2-1-OH α-naphthyl urethane, 58311-98-1; 2-CH_3O-1-OH, 58311-99-2; 2-CH_3O-1-OH TNB complex, 58312-00-8; 2-CH_3-1-OH, 58312-01-9; 2-CH_3-1-OH TNB complex, 58312-02-0; 2-Cl-1-OH, 58343-23-0; 2-Cl-1-OH TNB complex, 58343-24-1; 2-Br-1-OH, 58312-03-1; 2-Br-1-OH TNB complex, 58312-04-2; 2-I-1-OH, 58312-05-3; 2-CN-1-OH, 58312-06-4; 6-CH_3O-1-OH, 35046-06-1; 6-Br-1-OH, 35096-49-2; 6-CN-1-OH, 58312-07-5; 6-CN-1-OH TNB complex, 58312-08-6; 1-OAc, 26154-65-4; 1-OAc TNB complex, 58312-09-7; 3-SCN-1-OAc, 58312-10-0; 3-CH_3S-1-OAc, 58312-11-1; 3-CH_3S-1-OAc TNB complex, 58312-12-2; 3-Br-1-OAc, 58312-13-3; 3-Br-1-OAc TNB complex, 58312-14-4; 3-CH_3CO-1-OAc, 58312-15-5; 3-CH_3CO-1-OAc TNB complex, 58312-16-6; 3-CN-1-OAc, 58312-17-7; 3-NO_2-1-OAc, 58312-18-8; 2-CH_3O-1-OAc, 58312-19-9; 2-CH_3O-1-OAc TNB complex, 58312-20-2; 2-Br-1-OAc, 58312-21-3; 2-Br-1-OAc TNB complex, 58312-22-4; 2-I-1-OAc, 58312-23-5; 2-CN-1-OAc, 58312-24-6; 2-CN-1-OAc TNB complex, 58312-25-7; 6-CH_3-1-OAc, 58312-26-8; 6-CH_3-1-OAc TNB complex, 58312-27-9; 6-CN-1-OAc, 58312-28-0; 6-CN-1-OAc TNB complex, 58312-29-1; 6-Br-1-OAc, 58312-30-4; 1-OTs, 26154-60-9; 1-OTs TNB complex, 58312-31-5; 3-CH_3O-1-OTs, 58312-32-6; 3-CH_3O-1-OTs TNB complex, 58312-33-7; 3-CH_3-1-OTs, 58312-34-8; 3-CH_3-1-OTs TNB complex, 58312-35-9; 3-CH_3S-1-OTs, 33318-68-2; 3-CH_3S-1-OTs TNB complex, 58312-36-0; 3-Br-1-OTs, 33318-67-1; 3-Br-1-OTs TNB complex, 58312-37-1; 3-CH_3CO-1-OTs, 26154-62-1; 3-CN-1-OTs, 58312-38-2; 3-NO_2-1-OTs, 26154-61-0; 2-CH_3O-1-OTs, 58312-39-3; 2-CH_3O-1-OTs TNB complex, 58312-40-6; 2-CH_3-1-OTs, 58312-41-7; 2-CH_3-1-OTs TNB complex, 58312-42-8; 2-Cl-1-OTs, 58312-43-9; 2-Cl-1-OTs TNB complex, 58312-44-0; 2-Br-1-OTs, 58312-45-1; 2-Br-1-OTs TNB complex, 58312-46-2; 2-CN-1-OTs, 58312-47-3; 6-CH_3O-1-OTs, 58312-48-4; 6-CH_3O-1-OTs TNB complex, 58312-49-5; 6-CH_3-1-OTs, 58312-50-8; 6-CH_3-1-OTs TNB complex, 58312-51-9; 6-Br-1-OTs, 58312-52-0; 6-CN-1-OTs, 58312-53-1; **3**, 3806-02-8; **4** (R = CH_3; X = CH_3O), 734-61-2; **4** (R = C_2H_5; X = Cl), 36044-40-3; **4** (R = C_2H_5; X - Br), 58312-54-2; **4** (R = H; X = Br), 58312-55-3; **5** (X = CH_3O), 36044-37-8; **5** (X = CH_3), 769-86-8; **5** (X = CH_3) TNB complex, 58312-56-4; **5** (X = Cl), 36044-31-2; **5** (X = Br), 58312-57-5; **5** (X = I), 36044-41-4; **6**, 50469-71-1; **7**, 1157-45-5; **10** (R = H; X = CH_3O), 58312-58-6; **10** (R = H; X = Br), 33828-73-8; **12**, 53535-54-9; **16**, 35046-05-0; **17**, 35046-03-8; **21**, 58312-59-7; 1-azulylmethyltrimethylammonium idoide, 40450-20-2; 1-azulylacetonitrile, 53271-95-7; 1-azulylacetic acid, 26157-12-0; *p*-toluenesulfonyl chloride, 98-59-9; 1-azulyl benzoate, 58312-60-0; azulene, 275-51-4; benzoyl peroxide, 94-36-0; 1,3-azulene dibenzoate, 58312-61-1; 1-methoxyazulene, 30264-97-2; 1-methoxyazulene TNB complex, 58312-62-2; *N,N,N',N'*-tetramethyldiaminomethane, 51-80-9; (3-methoxy-1-azulylmethyl)trimethylammonium iodide, 58312-63-3; 3-methoxy-1-azulylacetonitrile, 58312-64-4; 3-methoxy-1-azulylacetic acid, 58312-65-5; (3-methyl-1-azulylmethyl)trimethylammonium iodide, 58312-66-6; tetranitromethane, 509-14-8; 1,3-bis(2-hydroxyethyl)-2-methylazulene, 58312-67-7; 1,3-bis(2-hydroxyethyl)-2-methylazulene TNB complex, 58312-68-8; bis(2-chloro-1-azulyl)methane, 58312-69-9; bis(2-bromo-1-azulyl)methane, 58312-70-2; 6-cyanoazulene, 58312-71-3.

Supplementary Material Available. Principal ir, full NMR, and uv–visible data for the compounds so designated (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) For part XI see R. N. McDonald and J. M. Richmond, *J. Org. Chem.*, **40**, 1689 (1975). (b) ACS–PRF Graduate Fellow, 1968–1969. (c) Phillips Petroleum Co. Fellowship, 1968–1969. (d) NSF Undergraduate Participant, 1969–1970.

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