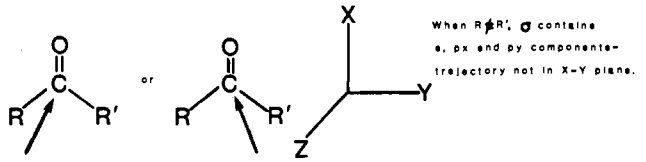

Figure 6. ϕ trajectories of nucleophiles at unsymmetrical π-electrophilic centers.

orthogonal to the λ-component.

Three-Dimensional Trajectory Terms. If the π-center undergoing nucleophilic attack (Figure 6) is located in a molecular environment having a symmetrical distribution of nuclei with respect to the x,z plane (ethylene, formaldehyde, acetylene), the θ's as defined by eq 2 and 4 are sufficient to describe the trajectory since the pertinent frontier σ^* and σ molecular orbitals contains only s and p_x components. Thus, the trajectory will be in the x,z plane. If, however, the π-center is located in a molecular environment having an asymmetric distribution of nuclei with respect to the x,z plane (propylene, acetaldehyde), the pertinent frontier σ^* and σ molecular orbitals will contain contributions from p_y as well as from p_x. Thus, the resulting nucleophile trajectory will contain x, y, and z vector components. The in-plane p-component of σ^* and σ are now described by the functions ($c_{p_x^*} \cos\phi + c_{p_y^*} \sin\phi$) and ($c_{p_x} \cos\phi + c_{p_y} \sin\phi$) in place of the $c_{p_x^*}$ and c_{p_x} terms, respectively, in eq 2 and 4. The resulting equations represent the expression required to complete the three-dimensional analysis of the θ trajectory on the frontier molecular orbital levels. The resulting trajectory angles θ and ϕ may be estimated by combining the differential equations describing the stabilizing two-electron and destabilizing four-electron terms ($d\Delta E_{ct}/d\theta$, $d\Delta E_{ct}/d\phi$, $d\Delta E_r/d\theta$, and $d\Delta E_r/d\phi$) and solving by an iterative procedure. Values of c_{s^*}, $c_{p_x^*}$, $c_{p_y^*}$, $c_{p_z^*}$, c_s, c_{p_x}, c_{p_y}, c_{p_z}, E_{π^*}, E_π, E_{σ^*}, and E_σ may be obtained from semiempirical molecular orbital calculations performed on a given π-electrophile. E_N can be determined from a similar calculation performed on a given nucleophile. The resonance integrals, β_s and β_p, may be easily estimated by the procedures suggested by Mulliken[12] and Hoffmann[13] using the ionization potentials of a carbon 2s electron (-21.85 ev), a carbon 2p electron (-12.05 ev), and an electron in the highest occupied molecular orbital of the nucleophile (α_N), and the σ-overlap integrals $(S_{i,j})_\sigma$ describing the interaction of a p orbital on the nucleophile with 2p $(S_{2p,2p})\sigma$ and 2s $(S_{2p,2s})\sigma$ orbitals on carbon. The values for the overlaps ($S_{i,j}$) may be easily determined from the tables listed in a publication by Mulliken, Rieke, Orloff, and Orloff.[14]

In a similar fashion eq 5 and 6 may be derived. These represent

$$\cos\theta_{ct} = \frac{\sum \frac{c_{s^*} c_{p_x^*}}{E_N - E_{\sigma^*}}}{\sum \frac{c_{p_z^*}^2}{E_N - E_{\pi^*}} - \sum \frac{c_{p_x}^2}{E_N - E_{\sigma^*}}} (\beta_s/\beta_p) \qquad (5)$$

$$\sin\theta_r = \frac{\sum c_s c_{p_x}}{\sum c_{p_z}^2 - \sum c_{p_x}^2} 0.5[(\beta_s/\beta_p) - (S_{sp}/S_{pp})] \qquad (6)$$

a more complete view of the two-electron and four-electron components in this trajectory analysis since *all* unoccupied and occupied molecular orbitals are included.

Conclusions

The following generalizations may be deduced from the proposed model: (1) Both the stabilizing two-electron and destabilizing four-electron minimum-energy trajectory angles, θ_{ct} and θ_r, respectively, are independent of the magnitude of the orbital coefficient associated with the nucleophile. (2) θ_r is independent of both the energy level of the nucleophile HOMO and the energy levels of the occuppied molecular orbitals of the π-electrophile. (3) For a given π-electrophile, as the energy of the frontier molecular orbital of the nucleophile (HOMO) becomes less negative, θ approaches 90°. Thus, hard nucleophiles (nucleophiles with low-lying HOMO's) would be expected to approach the reaction center of a given substrate at a smaller angle than corresponding soft nucleophiles (nucleophiles with higher lying HOMO's).

In conclusion, a simple model based upon the analysis of the first-order interactions between the highest filled molecular orbital on a nucleophile and all unoccupied and occupied molecular orbitals on the π-electrophile has been proposed for qualitatively predicting the trajectory of an attacking nucleophilic reagent with respect to a particular π-electrophilic center.

Acknowledgment. We thank the National Science Foundation, Department of Energy, and the National Institutes of Health for grants that supported this investigation.

(12) Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 295.
(13) Hoffmann, R. *J. Phys. Chem.* **1963**, *39*, 1397.
(14) Mulliken, R. W.; Rieke, C. A.; Orloff, D.; Orloff, H. *J. Chem. Phys.* **1949**, *17*, 1248.

Quinones of Azulene. 3. Generation and Trapping of the Reactive 1,4- and 1,6-Quinones[1]

Lawrence T. Scott,* Peter Grütter, and Raymond E. Chamberlain, III

Contribution from the Department of Chemistry, University of Nevada, Reno, Nevada 89557.
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Abstract: The 1,4-quinone of azulene (**1**) and the 1,6-quinone of azulene (**2**) have been synthesized for the first time. Oxidation of bicyclic trienone **3** followed by acetylation provides the two azulene diacetates **7** and **8** which serve as ideal precursors for the quinones. Neither quinone could be isolated in monomeric form, but both could be efficiently trapped by cyclopentadiene to give stable Diels-Alder adducts (**13** and **15**). The high chemical reactivity of azuloquinones **1** and **2** was anticipated on the basis of earlier theoretical calculations.

Nearly 50 years have elapsed since the first synthesis of azulene,[2] and the roots of quinone chemistry can be traced back to antiquity.[3] Why, then, is so little known about the quinones of azulene which lie at the intersection of these two venerable avenues

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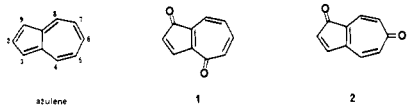
of research? A few substituted[4] and annelated[5] derivatives have been prepared, but not a single unadorned member of this intriguing family of compounds was reported prior to 1980.[6]

Struck by the lack of experimental data, several research groups joined together in the late 1970's to carry out extensive theoretical calculations on all 11 of the possible azuloquinones.[7] There emerged from this work the prediction, inter alia, that while many of these compounds should be highly reactive, some should be stable enough to isolate and characterize under ordinary laboratory conditions.[7] The truth, of course, can be established only by synthesizing these nonbenzenoid quinones.

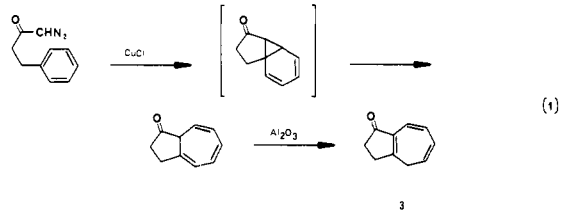
When contemplating how such compounds might be prepared, one naturally thinks of the traditional routes to quinones which culminate in oxidation of the corresponding hydroquinones.[3] Unfortunately, most of the known pathways to azulenes[8] appear unsuitable for the efficient preparation of doubly oxygenated azulenes, i.e., simple hydroquinones or their derivatives. It is this shortcoming of synthetic methodology, we believe, which has delayed for decades the preparation of azuloquinones. In this paper, we describe a new approach to oxygenated azulenes which has led to short syntheses of 1,4-azuloquinone (**1**) and 1,6-azuloquinone (**2**). As anticipated from the calculations,[7] both of these



previously unknown quinones proved to be highly reactive, but both could be trapped as transient species. In the following paper,[9] we describe the first syntheses of the parent 1,5- and 1,7-quinones of azulene, both of which can be isolated as stable, yellow, crystalline solids, likewise in agreement with theory.[7]

Syntheses

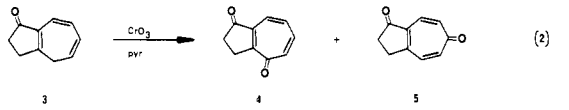
For construction of the bicyclo[5.3.0]decane ring system, we have relied on the intramolecular carbene addition reaction (eq 1) developed previously in our laboratory.[10] Recent improvements



(1)

in the experimental procedure now permit routine preparation of bicyclic trienone **3** on a 20–30-g scale.

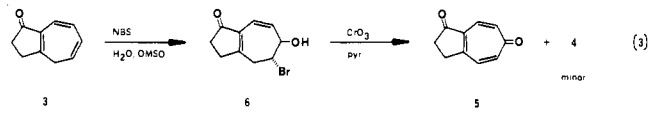
Oxidation of **3** with chromium trioxide–pyridine gives the two isomeric tropones **4** and **5** in roughly equal amounts (eq 2).[11] The



(2)

formation of **5** in this reaction was not unexpected, since double-bond migrations often accompany such allylic oxidations.[12] Obviously **4** and **5** both represent attractive intermediates for our purposes, and their separation presented no difficultly.

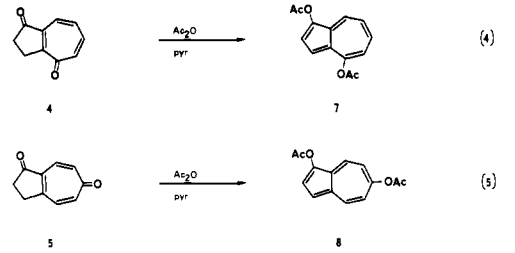
Although undeniably direct, introduction of a second oxygen atom onto the azulene framework as in eq 2 affords the two tropones **4** and **5** in a combined isolated yield of only 30–35%. A far superior method for the preparation of isomer **5** (73% yield) is illustrated in eq 3. Thus bromination of trienone **3** with



(3)

N-bromosuccinimide (NBS) in aqueous dimethyl sulfoxide (Me_2SO) gives a single bromohydrin to which we assign structure **6** on the basis of its ^1H NMR spectrum. Elimination of HBr and oxidation then leads to tropone **5**, accompanied by a small amount of **4**. The minor isomer presumably arises by allylic rearrangement after loss of HBr, either prior to or during the oxidation step.

Attempts to introduce a double bond directly into the five-membered ring of these 2,3-dihydroquinones by conventional methods (bromination, selenylation, DDQ oxidation, etc.) met with little success,[13] so more circuitous procedures were developed. Toward this end, it was found that the diketones **4** and **5** can be conveniently transformed into the beautiful blue azulene diacetates **7** and **8**, respectively, simply by stirring with acetic anhydride and pyridine in hot ethyl acetate (eq 4 and 5). The success of this



(4)

(5)

reaction most likely stems from the unusually high nucleophilicity of the tropone carbonyl oxygen, for enol acetates oridinarily cannot be prepared from ketones under these conditions. Enolization of the second carbonyl group is then facilitated by completion of the aromatic 10-electron π system of azulene. By these reactions, the doubly oxygenated azulenes **7** and **8** are now readily accessible.

On treatment with an excess of methyllithium in tetrahydrofuran (THF), 1,6-diacetoxyazulene (**8**) yields an emerald green solution of the azulene-1,6-hydroquinone dianion (**9**) by nucleophilic cleavage of the ester groups. Unfortunately, neutralization of this solution with acetic acid affords not the corresponding hydroquinone **10** but rather the diketo tautomer **5** from which diacetate **8** was originally derived (eq 6). Apparently, the aromaticity of azulene does not suffice to overcome the strength of two carbonyl π bonds and any special thermodynamic stability associated with the tropone ring.[14]

(1) For preceding papers in this series on "The Quinones of Azulene", see: Scott, L. T. *Pure Appl. Chem.* **1983**, *55*, 363–368, and ref 7. Preliminary accounts of this work have been presented at the International Symposium on Theoretical Organic Chemistry, Dubrovnik, Yugoslavia, Aug 30–Sept 3, 1982, and at the 185th National Meeting of the American Chemical Society, Seattle, Wash., March 21–25, 1983.

(2) Plattner, P. A.; Pfau, A. S. *Helv. Chim. Acta* **1937**, *20*, 224–232.

(3) Patai, S., Ed. "The Chemistry of Quinonoid Compounds"; Wiley-Interscience: New York, 1974; Vol 1 and 2. Thomson, R. H. "Naturally Occurring Quinones"; Academic Press: New York, 1971.

(4) Morita, T.; Takase, K. *Chem. Lett.* **1977**, 513–516. Morita, T.; Ise, F.; Takase, K. *Ibid.* **1982**, 1303–1306. See also ref 6.

(5) Marisli, A.; Isola, M. *Tetrahedron Lett.* **1965**, 3023–3026. Ried, W.; Ehret, J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 377–378. Munday, R.; Sutherland, I. O. *J. Chem. Soc. C* **1969**, 1427–1434. Hafner, K.; Meinhardt, K.-P.; Richarz, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 204–205.

(6) The 1,2-quinone of azulene and derivatives thereof have been reported by: Morita, T.; Karasawa, M.; Takase, K. *Chem. Lett.* **1980**, 197–200.

(7) Scott, L. T.; Rozeboom, M. D.; Houk, K. N.; Fukunaga, T.; Lindner, H. J.; Hafner, K. *J. Am. Chem. Soc.* **1980**, *102*, 5169–5176.

(8) Keller-Schierlein, W.; Heilbronner, E. In "Non-Benzenoid Aromatic Compounds"; Ginsburg, D., Ed.; Interscience: New York, 1959; pp 237–277. Mukherjee, D.; Dunn, L. C.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 251–2, and references cited therein.

(9) Scott, L. T.; Adams, C. M. *J. Am. Chem. Soc.*, following paper in this issue.

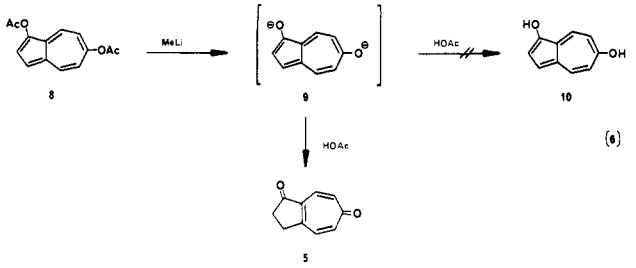
(10) Scott, L. T.; Minton, M. A.; Kirms, M. A. *J. Am. Chem. Soc.* **1980**, *102*, 6311–6314.

(11) Tropone **5** has previously been reported as a by-product (8% yield) from the cyclization of 4-(*p*-hydroxyphenyl)-1-diazo-2-butanone according to the reaction in eq 1: Iwata, C.; Yamada, M.; Shinoo, Y.; Kobayashi, K.; Okada, H. *J. Chem. Soc., Chem. Commun.* **1977**, 888–889.

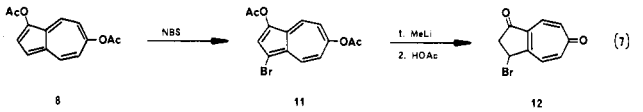
(12) Wiberg, K. B.; Nielsen, S. D. *J. Org. Chem.* **1964**, *29*, 3353.

(13) Bromination of **5** with NBS and benzoyl peroxide in carbon tetrachloride followed by treatment of the crude reaction mixture with excess pyridine and cyclopentadiene did give the Diels–Alder adduct **13** in low yield. Attempts to isolate the intermediate bromide, however, yielded only polymers.

(14) For discussions on the aromaticity of azulene and of tropone, see: Badger, G. M. "Aromatic Character and Aromaticity"; Cambridge University Press: Cambridge, 1969.

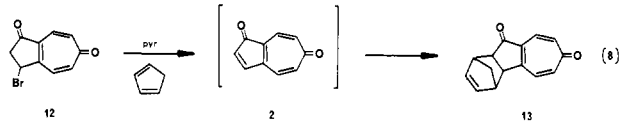


Conversion of diketone **5** to diacetate **8** and then back again (eq 5 and 6) hardly seems very useful on first inspection. We have devised a scheme, however, to take advantage of this reaction cycle by interjecting an additional step at the azulene stage. Thus, bromination of the diacetoxyazulene **8** with NBS proceeds in the anticipated manner[15] to produce the 3-bromo derivative **11**. Now, cleavage of the acetate groups with methyllithium, followed by neutralization with acetic acid, yields the bromo diketone **12** (eq 7). The problems encountered earlier with direct introduction



of heteroatom substituents onto the cyclopentenone ring of **5** can thereby be neatly circumvented.

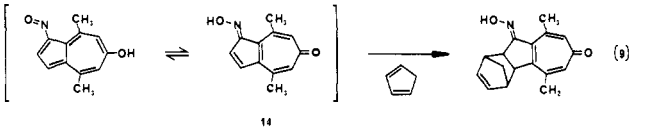
The final elimination of HBr from **12** occurs under extremely mild conditions. Addition of **12** to a solution of pyridine and cyclopentadiene smoothly generates the 1,6-quinone of azulene (**2**), and this reactive species is immediately trapped in a Diels–Alder reaction (eq 8). Cycloadduct **13** can be isolated in 64%



overall yield from 1,6-diacetoxyazulene (**8**) and exhibits spectroscopic properties closely resembling those of dione **5**. An endo stereochemistry best accounts for the observed ^{1}H NMR coupling constants.

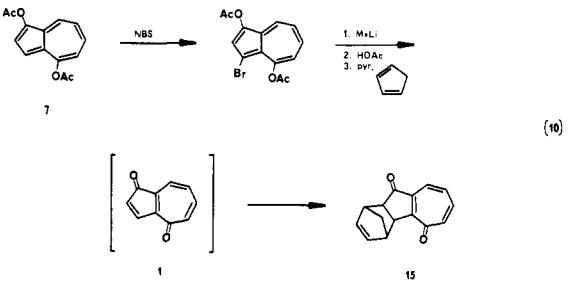
Omission of the cyclopentadiene from this reaction has not yet permitted isolation of the monomeric quinone (**2**); under the conditions explored to date, an unstable purple compound is formed which may be dimeric but has resisted complete characterization.

Unpublished experiments from the laboratory of Professor Hafner in Darmstadt[16] have established that compound **14**, the oxime of a 1,6-azuloquinone obtained by nitrosation of 4,8-dimethyl-6-hydroxyazulene, behaves in a completely analogous manner (eq 9).

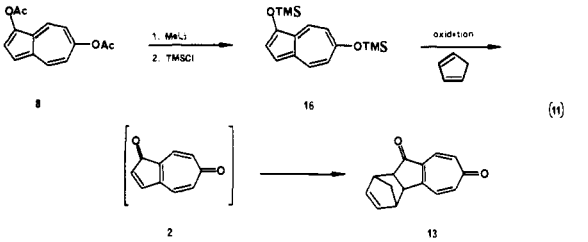


The 1,4-quinone of azulene (**1**) has likewise proven too reactive to isolate in monomeric form under normal conditions, but it can be synthesized by the same reaction sequence which has led to the 1,6 isomer. Thus, bromination of 1,4-diacetoxyazulene (**7**) followed by cleavage with methyllithium, neutralization, and HBr elimination as described above generates 1,4-azuloquinone (**1**) which can be trapped by cyclopentadiene to give the Diels–Alder adduct **15** (eq 10).

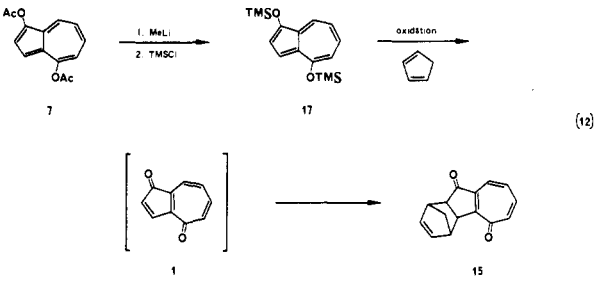
As an alternative to the bromination–dehydrobromination pathway, we have developed a second method for generating



azuloquinones, the last step of which can be executed under strictly neutral conditions. This method involves bis(trimethylsilyl) ethers of azulene hydroquinones, such as **16**, which can be prepared simply by quenching the corresponding hydroquinone dianions with chlorotrimethylsilane.[17] Oxidation of **16** to the 1,6-azuloquinone (**2**), if carried out in the presence of cyclopentadiene, leads to the same Diels–Alder adduct obtained before (eq 11). This



method has also been applied to the generation of 1,4-azuloquinone (eq 12). Useful oxidizing agents in these reactions include py-



ridinium chlorochromate (PCC)[18] and tetrachloro-*p*-benzoquinone (*p*-chloranil).

To summarize, both 1,4-diacetoxyazulene (**7**) and 1,6-diacetoxyazulene (**8**) have been prepared, each in two steps, from the readily available bicyclic trienone **3**. Each in turn has then been transformed into the corresponding quinone of azulene by two distinct routes.

Properties

Since the title compounds enjoy only a fleeting existence, even in dilute solution under neutral conditions, it has not yet been possible to examine them by the customary spectroscopic methods. Nevertheless, certain conclusions about their properties can be drawn from other observations. It is quite clear, for example, that azuloquinones **1** and **2** both exhibit high reactivity as dienophiles in the Diels–Alder reaction. Their cycloadditions with cyclopentadiene at 0 °C must occur quite rapidly in order to compete so successfully with the alternative bimolecular processes which preclude their isolation. From the calculations we published in 1980, it was expected that azuloquinones **1** and **2** should be at least as dienophilic as *p*-benzoquinone, if not more so.[7]

The fact that an oxidizing agent no more powerful than *p*-chloranil ($E_{1/2}$ = +0.01 V)[3] can effect the final transformations

(15) Anderson, A. G., Jr.; Nelson, J. A.; Tazuma, J. T. *J. Am. Chem. Soc.* **1953**, *75*, 4980–4989.

(16) Grund, A. Dr.-Ing. Dissertation, Technischen Hochschule Darmstadt, West Germany, 1980. We thank Professor Hafner for permission to cite this work.

(17) Direct synthesis of **16** from diketone **5** with iodotrimethylsilane and hexamethyldisilazane according to the procedure of Miller, R. D.; McKean, D. R. (*Synthesis* **1979**, 730–732), although marginally successful, proved inferior to the route via diacetate **8**. Attempts to generate dianion **9** by deprotonation of diketone **5** under a variety of conditions (e.g., LDA, −78 °C) failed completely.

(18) Willis, J. P.; Gogins, K. A. Z.; Miller, L. L. *J. Org. Chem.* **1981**, *46*, 3215–3218.

depicted in eq 11 and 12 provides valuable information about the redox properties of these azuloquinones. Specifically, the potential of 1,4-azuloquinone (**1**) and that of 1,6-azuloquinone (**2**) must fall below that of *p*-chloranil; i.e. $E_{1/2} < +0.01$ V. This conclusion also stands in harmony with predictions based on the published calculations.[7] Experiments aimed at the direct spectroscopic detection and study of 1,4- and 1,6-azuloquinones have been initiated.

Experimental Section

General. Tetrahydrofuran (THF) and ether were dried by distillation under nitrogen from the sodium ketyl of benzophenone immediately prior to use. Baker silica gel 60–200 was used for all column chromatography, and Woelm silica gel F was use for preparative layer chromatography. All ^{13}C NMR spectra were recorded at 25 MHz on a JEOL FX100 instrument; ^1H NMR spectra were recorded on the same instrument (100 MHz) or on an Hitachi Perkin-Elmer R24B spectrometer (60 MHz); chemical shifts are reported in ppm downfield from tetramethylsilane. Combustion analyses were performed by Spang, Eagle Harbor, MI, and high resolution mass spectra were recorded at the Midwest Center for Mass Spectrometry, Lincoln, NB (NSF Regional Facility). Melting points are uncorrected.

3,4-Dihydro-1(2*H*)-azulenone (3). The procedure we described previously[10] for the preparation of this bicyclic trienone can be carried out more conveniently and in higher yield by substituting 1,2-dichloroethane for bromobenzene and running the reaction at reflux. From 10.0 g of 1-diazo-4-phenyl-2-butanone (1.5 L of 1,2-dichloroethane) there was obtained 5.9 g (71% yield) of **3** after purification by this procedure. If the reaction is performed at higher concentrations, much larger quantities of **3** can be prepared in a single run, albeit in somewhat diminished percent yield. Thus, 41.3 g of the diazo ketone (4.5 L of 1,2-dichloroethane) gave 19.8 g (57% yield) of **3**. The properties of bicyclic trienone **3** have been reported elsewhere.[10]

2,3-Dihdyro-1,4-azulenedione (4) and 2,3-Dihydro-1,6-azulenedione (5). Method A.[19] To a solution of 300 mL of methylene chloride and 25 mL of pyridine under nitrogen was added 15 g (150 mmol) of chromium trioxide with vigorous stirring at 0 °C. After 15 min, 1.46 g (10 mmol) of trienone **3** was added, and the cold bath was removed. Stirring was continued for 24 h at room temperature. The reaction mixture was then filtered through Celite, washed with 3 × 50 mL of 5% HCl, and washed once with 50 mL of saturated aqueous NaCl. The combined aqueous layers were extracted several times with methylene chloride. After drying over $MgSO_4$, the combined organic layers were concentrated under reduced pressure. Flash chloromatography[20] of the crude product mixture on silica gel with 1:1 ethyl acetate/petroleum ether gave 282 mg (18%) of **4** and 257 mg (16%) of **5** both was light-brown solids; the 1,4 isomer (**4**) was eluted from the column first. For subsequent reactions, the chromatographically purified materials proved satisfactory; however, analytically pure samples were prepared by crystallization from hexane/methylene chloride followed by sublimation at 60 °C (ca. 10^{-5} torr).

4: light yellow crystals; mp 119 °C; ^1H NMR ($CDCl_3$) δ 7.4–6.9 (m, 4), 2.99 (dd, J = 8.0 and 5.5 Hz), 2.63 (dd, 2, J = 8.0 and 5.5 Hz); ^{13}C NMR ($CDCl_3$) δ 207.8, 185.1, 168.2, 140.1, 139.8, 137.1, 133.0, 127.6, 33.3, 2.60; IR ($CHCl_3$) 1728 (s), 1630 (w), 1590 (s), 1538 (w) cm^{-1}; UV max (EtOH) 325 (log ϵ 3.93), 233 nm (4.35). Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 74.99; H, 5.14.

5: light yellow crystals; mp 131 °C (lit.[11] mp 125–126 °C); ^1H NMR ($CDCl_3$) δ 7.1 (m, 4), 3.0 (m, 4); ^{13}C NMR ($CDCl_3$) δ 205.4, 187.2, 165.0, 144.5, 139.8, 139.1, 134.7, 129.3, 34.0, 29.5; IR ($CHCl_3$) 1713 (s), 1633 (s), 1613 (s), 1579 (s), 1549 (m) cm^{-1}; UV max (EtOH) 316 (log ϵ 3.95), 309 (sh), 240 (sh), 233 nm (4.37). Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 74.84; H, 5.03.

Method B. To a solution of 1.46 g (10 mmol) of trienone **3** and 0.18 mL (10 mmol) of water in 25 mL of dimethyl sulfoxide (DMSO) under nitrogen was added 1.78 g (10 mmol) of *N*-bromosuccinimide (NBS) with stirring at 10 °C. After the addition of NBS, the cold bath was removed, and stirring was continued for 40 min as the reaction mixture warmed to room temperature. Dilution of the reaction mixture with 100 mL of methylene chloride gave a solution which was washed with 2 × 50 mL of 5% aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure. The unstable bromohydrin **6** thus obtained was used promptly, without purification, in the next step.

To a solution of 150 mL of methylene chloride and 12.5 mL of pyridine under nitrogen was added 7.5 g (75 mmol) of chromium trioxide with vigorous stirring at 0 °C. After 15 min, a solution of the crude bromohydrin **6** (from above) in 20 mL of methylene chloride was added, and the cold bath was removed. Stirring was continued for 19 h at room temperature. Workup as in method A gave 0.112 g (7%) of **4** and 1.166 g (73%) of **5** after chromatography.

1,4-Diacetoxyazulene (7). A solution of 160 mg (1.0 mmol) of dione **4**, 1 mL of acetic anhydride, and 2 mL of pyridine in 20 mL of ethyl acetate was refluxed under nitrogen for 10 h. The reaction mixture was then cooled to room temperature; diluted with 40 mL of ether; washed successively with 2 × 40 mL of 2% aqueous HCl, 2 × 40 mL of 5% aqueous sodium bicarbonate, and once with 40 mL of saturated aqueous NaCl; dried over $MgSO_4$; and concentrated under reduced pressure. Flash chromatography[20] of the crude product mixture on silica gel with ethyl acetate/petroleum ether (initially 1:10 but with a gradual increase in the proportion of ethyl acetate) gave 149 mg (61%) of **7** and 54 mg (34%) of recovered starting material **4**. The yield of **7** based on unrecovered starting material (92%) was not improved by longer reaction times. Recrystallization of **7** from hexane/methylene chloride gave analytically pure material: pure crystals, mp 75–76 °C; ^1H NMR ($CDCl_3$) δ 8.03 (d, 1, J = 9.5 Hz), 7.55 (d, 1, J = 3.5 Hz), 7.37 (t, 1, J = 9.5 Hz), 7.04 (d, 1, J = 3.5 Hz), 6.85 (t, 1, J = 9.5 Hz), 6.76 (d, 1, J = 9.5 Hz), 2.37 (s, 3), 2.32 (s, 3); ^{13}C NMR ($CDCl_3$) δ 168.9, 168.7, 154.2, 138.6, 136.3, 132.4, 127.0, 126.2, 125.5, 120.7, 118.7, 109.7, 21.5, 20.1; IR ($CHCl_3$) 1760 (s), 1727 (sh), 1584 (m), 1501 (m) cm^{-1}; UV max (cyclohexane) 716 (sh, log ϵ 2.05), 648 (sh, 2.44), 598 (2.49), 368 (3.52), 359 (3.46), 350 (3.68), 335 (3.56), 281 (4.66), 240 nm (4.42), (acetonitrile) 592 nm (2.31). Anal. Calcd for $C_{14}H_{12}O_4$ C, 68.85; H, 4.95. Found: C, 69.00; H, 4.95.

1,6-Diacetoxyazulene (8). A solution of 480 mg (3 mmol) of dione **5**, 1.5 mL of acetic anhydride, and 3 mL of pyridine in 20 mL of ethyl acetate was refluxed under nitrogen for 26 h. The reaction mixture was then cooled to room temperature; diluted with 40 mL of ether; washed successively with 3 × 30 mL of 2% aqueous HCl, 2 × 40 mL of 5% aqueous sodium bicarbonate, and once with 40 mL of saturated aqueous NaCl; dried over $MgSO_4$; and concentrated under reduced pressure. Flash chromatography[20] of the crude product mixture on silica gel with ethyl acetate/petroleum ether (initially 1:8 but with a gradual increase in the proportion of ethyl acetate) gave 463 mg (63%) of **8** and 106 mg (22%) of recovered starting material **5**. The yield of **8** based on unrecovered **5** (81%) was not improved by longer reaction times. Recrystallization of **8** from hexane/methylene chloride gave analytically pure material: blue crystals, mp 93 °C; ^1H NMR ($CDCl_3$) δ 7.96 (br d, 2, J = 10.2 Hz), 7.60 (d, 1, J = 4.0 Hz), 7.10 (d, 1, J = 4.0 Hz), 6.65 (br d, 2, J = 10.2 Hz), 2.30 (s, 3), 2.23 (s, 3); ^{13}C NMR ($CDCl_3$) δ 169.9, 169.3, 157.9, 139.1, 136.2, 133.7, 130.7, 127.3, 124.5, 116.7, 116.5, 115.5, 21.1, 20.9; IR ($CHCl_3$) 1763 (s), 1590 (m), 1499 (m) cm^{-1}; UV max (cyclohexane) 722 (sh, log ϵ 2.10), 652 (sh, 2.51), 599 (2.58), 369 (3.39), 351 (3.72), 336 (3.61), 282 (4.78), 236 nm (4.19), (acetonitrile) 595 nm (2.45). Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.74; H, 4.91.

Generation and Protonation of Azulene-1,6-hydroquinone Dianion (9). A solution of 38 mg (0.16 mmol) of 1,6-diacetoxyazulene (**8**) in 20 mL of ether was added dropwise with stirring under nitrogen to 20 mL of cold (0 °C) ether containing 0.43 mL (0.69 mmol) of a methyllithium solution (1.6 M in ether). The theoretical stoichiometry for this reaction is 1:4. At the completion of the addition, the ice bath was removed, and stirring was continued for 10 min. The resulting emerald green solution was then quenched with 0.2 mL of glacial acetic acid, diluted with 10 mL of ethyl acetate, and filtered through Celite. Additional ethyl acetate was used to wash the Celite, and the combined organic solutions were evaporated to dryness under reduced pressure. Chromatography of the crude product on silica gel with 1:1 ethyl acetate/petroleum ether gave 18.5 mg (75%) of dione **5**.

3-Bromo-1,6-diacetoxyazulene (11). To a solution of 163 mg (0.66 mmol) of 1,6-diacetoxyazulene (**8**) in 15 mL of benzene was added 142 mg (0.80 mmol) of *N*-bromosuccinimide; the mixture was stirred under nitrogen for 12 h at room temperature. The reaction mixture was then diluted with 80 mL of ether, washed with 2 × 40 mL of water, dried over $MgSO_4$, and concentrated under reduced pressure. Flash chromatography[20] of the crude product on silica gel with 10:1 petroleum ether/ethyl acetate gave 204 mg (95%) of **11**. Recrystallization from hexane/methylene chloride gave blue crystals: mp 73 °C; ^1H NMR ($CDCl_3$) δ 7.99 (d, 1 J = 10.2 Hz), 7.85 (d, 1, J = 10.2 Hz), 7.57 (s, 1), 6.70 (dd, 1, J = 10.2 and 1.5 Hz), 6.67 (dd, 1, J = 10.2 and 1.5 Hz), 2.31 (s, 3), 2.28 (s, 3); IR ($CHCl_3$) 1767 (s), 1587 (m), 1497 (m) cm^{-1}; UV max (cyclohexane) 672 (sh), 624 (log ϵ 2.42), 377 (3.53), 368 (3.42), 358 (3.69), 343 (sh), 298 (4.57), 291 (4.56), 236 nm (4.11), (acetonitrile) 612 nm (2.57). Crystals of **11** decompose on standing.

***endo*-Tetracyclo[10.2.1.$0^{2,11}$.$0^{3,9}$]pentadeca-3(9),4,7,13-tetraene-6,10-dione (13), the Diels–Alder Adduct of 1,6-Azuloquinone (2), from 11 via 3-Bromo-2,3-dihydro-1,6-azulenedione (12).** To a solution of 107 mg

(19) This procedure is modeled after that reported by: Fullerton, D. S.; Chen, C. *Synth. Commun.* **1976**, *6*, 217.

(20) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(0.33 mmol) of 3-bromo-1,6-diacetoxyazulene in 30 mL of ether under nitrogen at 0 °C was added 20 mL of ether containing 0.92 mL (1.47 mmol) of a methyllithium solution (1.6 M in ether). After 10 min, the green reaction mixture was acidified with 0.15 mL (2.6 mmol) of glacial acetic acid. The resulting brown mixture, presumed to contain bromo dione **12**, was then added without delay to a solution of 0.2 mL of pyridine in 5 mL of freshly distilled cyclopentadiene. This reaction mixture was stirred for 20 min at room temperature and was then washed sequentially with 2 × 20 mL of water and 2 × 20 mL of 2% aqueous HCl. The combined aqueous layers were extracted with 3 × 30 mL of methylene chloride. All the organic solutions were then combined, dried over $MgSO_4$, and concentrated under reduced pressure. Preparative layer chromatography of the crude product mixture on silica gel with 3:1 ethyl acetate/petroleum ether gave 50 mg (67%) of **13** and 4 mg (7%) of 2,3-dihydro-1,6-azulenedione (**5**). Molecular distillation (80 °C, 10^{-5} torr) of **13** provided a pure sample as a thick yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.2–6.8 (m, 4), 5.82 (dd, 1, J = 5.0 and 2.8 Hz), 5.48 (dd, 1, J = 5.0 and 2.8 Hz), 3.64 (br t, 1, J = 5 Hz), 3.4–3.1 (m, 2), 3.00 (br t, 1, J = 5 Hz), 1.71 (br s, 2); ^{13}C NMR ($CDCl_3$) δ 206.6, 187.1, 165.5, 144.5, 141.1, 139.8, 133.9, 133.5, 132.0, 129.3, 52.5, 50.4, 48.1, 45.5, 44.9; IR ($CHCl_3$) 1711 (s), 1635 (s), 1617 (s), 1580 (s), 1549 (m) cm^{-1}; UV max (EtOH) 318 (sh), 308, 241 (sh), 235 nm. MS (M^+). Calcd for $C_{15}H_{12}O_2$: 224.0837. Found: 224.0835.

***endo*-Tetracyclo[10.2.1.0^{2,11}.0^{3,9}]pentadeca-3(9),5,7,13-tetraene-4,10-dione (15), the Diels-Alder Adduct of 1,4-Azuloquinone (1), from 7 via the Bromination Route.** To a solution of 81 mg (0.33 mmol) of 1,4-diacetoxyazulene (**7**) in 10 mL of carbon tetrachloride was added 71 mg (0.40 mmol) of *N*-bromosuccinimide; the mixture was stirred under nitrogen for 15 h at room temperature. The reaction mixture was then filtered and concentrated under reduced pressure to give the very unstable 3-bromo-1,4-diacetoxyazulene: ^{1}H NMR (CCl_4) δ 7.91 (d, 1, J = 9.5 Hz), 7.51 (s, 1), 7.18 (t, 1, J = 9.5 Hz), 6.64 (t, 1, J = 9.5 Hz), 6.50 (d, 1, J = 9.5 Hz), 2.31 (s, 3), 2.22 (s, 3); IR (CCl_4) 1768 (s), 1720 (m), 1575 (m), 1511 (m) cm^{-1}; UV max (cyclohexane) 670 (sh), 624, 372, 364, 354, 338 (sh), 288, 242 nm, (EtOH) 612 nm. This unpurified product was immediately dissolved in 30 mL of ether, and the resulting solution was cooled to 0 °C under nitrogen. Thereto was added 15 mL of ether containing 1.0 mL (1.6 mmol) of a methyllithium solution (1.6 M in ether). After 5 min, the green reaction mixture was acidified with 0.3 mL (5.2 mmol) of glacial acetic acid. The resulting purple-brown mixture, presumed to contain 3-bromo-2,3-dihydro-1,4-azulenedione, was then added without delay to a solution of 1.0 mL of pyridine in 5 mL of freshly distilled cyclopentadiene. This reaction mixture was stirred for 20 min at room temperature and was then washed sequentially with 2 × 20 mL of water and 3 × 20 mL of 2% aqueous HCl. The combined aqueous layers were extracted with 3 × 30 mL of methylene chloride; then all the organic solutions were combined, dried over $MgSO_4$, and concentrated under reduced pressure. Preparative layer chromatography of the crude product mixture on silica gel with 3:1 ethyl acetate/petroleum ether gave 19.2 mg (26% from 1,4-diacetoxyazulene (**7**)) of **15** and 3 mg (5%) of 2,3-dihydro-1,4-azulenedione (**4**). The adduct was obtained as a thick yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.3–6.9 (m, 4), 5.82 (dd, 1, J = 5.0 and 2.8 Hz), 5.52 (dd, 1, J = 5.0 and 2.8 Hz), 3.85 (br t, 1, J = 5 Hz), 3.6–3.4 (m, 1), 3.4–3.2 (m, 1), 3.06 (t, 1, J = 5 Hz), 1.71 (br s, 2); ^{13}C NMR ($CDCl_3$) δ 206.5, 185.4, 168.5, 142.5, 140.6, 137.3, 133.4 (2C), 132.9, 127.9, 52.3, 50.3, 45.8, 45.4, 44.7; IR ($CHCl_3$) 1718 (s), 1629 (w), 1586 (s), 1531 (w) cm^{-1}; UV max (EtOH) 327, 233 nm. MS (M^+). Calcd for $C_{15}H_{12}O_2$: 224.0837. Found: 224.0841.

***endo*-Tetracyclo[10.2.1.0^{2,11}.0^{3,9}]pentadeca-3(9),4,7,13-tetraene-6,10-dione (13), the Diels–Alder Adduct of 1,6-Azuloquinone (2), via 1,6-Bis(trimethylsilyloxy)azulene (16). Method A.** A solution of 79 mg (0.32 mmol) of 1,6-diacetoxyazulene (**8**) in 10 mL of THF was cooled to −78 °C under nitrogen. To this blue solution was added 10 mL of THF containing 1.0 mL (1.5 mmol) of a methyllithium solution (1.5 M in ether), dropwise with stirring. After 10 min at −78 °C, the solution appeared emerald green, as expected for the hydroquinone dianion **9**. To this solution was added 10 mL of THF containing 0.13 mL (1.03 mmol) of chlorotrimethylsilane. The solution immediately turned blue again, indicating formation of the bis(trimethylsilyl) ether **16**. After 10 min, 20 mL of freshly distilled cyclopentadiene was added. Stirring was continued at −78 °C for 5 min more; then 10 mL of THF containing 135 mg (0.5 mmol) of tetrachloro-*p*-benzoquinone (*p*-chloranil) was added dropwise. The resulting dark blue-green solution was allowed to warm to room temperature and was then washed sequentially with 3 × 25 mL of 5% aqueous HCl, 2 × 25 mL of water, and 2 × 25 mL of saturated aqueous NaCl. The organic layer was dried over $MgSO_4$ and concentrated at 30 °C under reduced pressure. To separate the desired product from dicyclopentadiene and some chloranil–cyclopentadiene Diels–Alder adduct, the crude product mixture was subjected to preparative layer chromatography on silica gel with 1:1 ethyl acetate/petroleum ether. There was thus obtained 42 mg (59%) of the previously characterized Diels–Alder adduct **13**.

Method B. A solution of 121 mg (0.50 mmol) of 1,6-diacetoxyazulene (**8**) in 20 mL of THF was cooled to −78 °C under nitrogen. To this blue solution was added 10 mL of THF containing 1.32 mL (2.0 mmol) of a methyllithium solution (1.5 M in ether), dropwise with stirring. After 10 min at −78 °C, the solution appeared emerald green, and 10 mL of THF containing 0.314 mL of chlorotrimethylsilane was added. The solution immediately turned blue again and was then concentrated at ambient temperature under reduced pressure. The crude product (**16**) was immediately redissolved in 10 mL of 1,2-dichloroethane, and the resulting blue solution was added dropwise to 25 mL of 1,2-dichloroethane containing 12 mL of freshly distilled cyclopentadiene and 139 mg (0.64 mmol) of pyridinium chlorochromate, with stirring at room temperature. Stirring was continued at room temperature for 30 min; then the mixture was concentrated at 30 °C under reduced pressure. Preparative layer chromatography on silica gel with 1:1 ethyl acetate/petroleum ether gave 61 mg (55%) of the previously characterized Diels–Alder adduct **13**. Method B, which uses a Cr(VI) oxidizing agent, offers the advantage of fewer organic by-products.

***endo*-Tetracyclo[10.2.1.0^{2,11}.0^{3,9}]pentadeca-3(9),5,7,13-tetraene-4,10-dione (15), the Diels–Alder Adduct of 1,4-Azuloquinone (1), via 1,6-Bis(trimethylsilyloxy)azulene. Method A.** A solution of 75 mg (0.31 mmol) of 1,4-diacetoxyazulene (**7**) in 25 mL of THF was cooled to 0 °C under nitrogen. To this blue solution was added 10 mL of THF containing 0.85 mL (1.28 mmol) of a methyllithium solution (1.5 M in ether), dropwise with stirring. During the course of 30 min at 0 °C, the reaction mixture changed color from blue to purple to red-brown to blue-green. To this solution was added 10 mL of THF containing 0.20 mL (1.6 mmol) of chlorotrimethylsilane. The reaction mixture was stirred at room temperature for 30 min, during which time the color changed back to a deep blue. Then, 10 mL of freshly distilled cyclopentadiene was added, and this was followed immediately by the dropwise addition of 10 mL of THF containing 100 mg (0.41 mmol) of tetrachloro-*p*-benzoquinone (*p*-chloranil) at room temperature. Stirring was continued for 1 h. The resulting reddish black solution was concentrated under reduced pressure to give a dark oil. Preparative layer chromatography on silica gel with 1:1 ethyl acetate/hexane gave 24 mg (35%) of the previously characterized Diels–Alder adduct **15**.

Method B. A solution of 87 mg (0.36 mmol) of 1,4-diacetoxyazulene (**7**) in 20 mL of THF was cooled to 0 °C under nitrogen. To this blue solution was added 10 mL of THF containing 1.0 mL (1.5 mmol) of a methyllithium solution (1.5 M in ether), dropwise with stirring. During the course of 15 min at 0 °C, the reaction mixture changed color from blue to purple to red-brown to blue-green. Cleavage of 1,4-diacetoxyazulene (**7**) to the hydroquinone dianion requires conditions significantly less mild (0 °C, 15 min) than those which proved adequate for the corresponding reaction of 1,6-diacetoxyazulene (**8**) (−78 °C, 10 min). The dianion was then quenched by adding 10 mL of THF containing 0.25 mL (2.0 mmol) of chlorotrimethylsilane with stirring. After an additional 15 min at 0 °C, the reaction mixture had returned to a blue color and was concentrated at ambient temperature under reduced pressure. The crude bis(trimethylsilyloxy)azulene was immediately redissolved in 10 mL of 1,2-dichloroethane, and the resulting blue solution was added dropwise to 40 mL of 1,2-dichloroethane containing 10 mL of freshly distilled cyclopentadiene and 110 mg (0.51 mmol) of pyridinium chlorochromate, with stirring at room temperature. Stirring was continued at room temperature for 60 min. The brown reaction mixture was then concentrated at 30 °C under reduced pressure. Preparative layer chromatography on silica gel with 1:1 ethyl acetate/hexane gave 46 mg (57%) of the previously characterized Diels–Alder adduct **15**.

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