A New Convenient Synthesis of 1,2′-Biazulenes by Photolysis of 2-Diazo-1,3-dicyanoazulen-6(2*H*)-one with Azulene Derivatives

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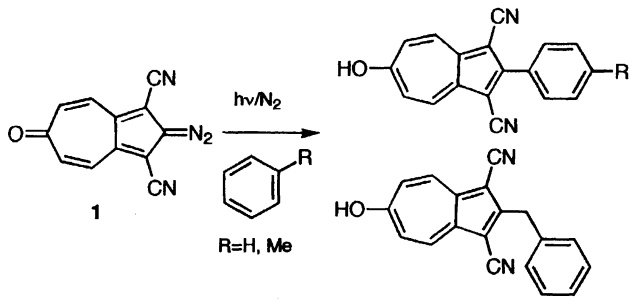
A photolysis of 2-diazo-1,3-dicyanoazulen-6(2*H*)-one in the presence of azulene derivatives in anhydrous ethyl acetate solution afforded 1,2′-biazulene derivatives, which are otherwise difficult to obtain, in good yields, nearly 90% or more. Accompanying by-products, 1,3-dicyanoazulen-6-ol and 2,5′-biazulene derivatives, were also characterized.

Due to the dipolar contribution of azulenes,[1,2] their 1, 3-positions are highly reactive with various electrophiles; known to date are halogenations, Vilsmeier reaction,[3] Friedel–Crafts reaction,[4] Michael additions,[5] and so on. However, an introduction of alkyl, aralkyl or aryl substituents to the 2-position has been difficult in practice. Since the first synthesis of biazulenes appeared in 1968,[6] there are a few other methods known, but they all suffered rather low yields,[7—10] so improved procedures are still called for. Meanwhile, we have found that the photolysis of 2-diazo-1, 3-dicyanoazulen-6(2*H*)-one (**1**, DAQ)[11] in various solvents, irrespective of protic or aprotic, resulted in an introduction of the solvent moiety into the 2-position of **1**; among the noteworthy findings therefrom is, along with a formation of 2,6-bridged oligomeric crown type ethers by photolyzing in tetrahydrofuran,[12] the arylation in benzene or in toluene (Scheme 1).[13]

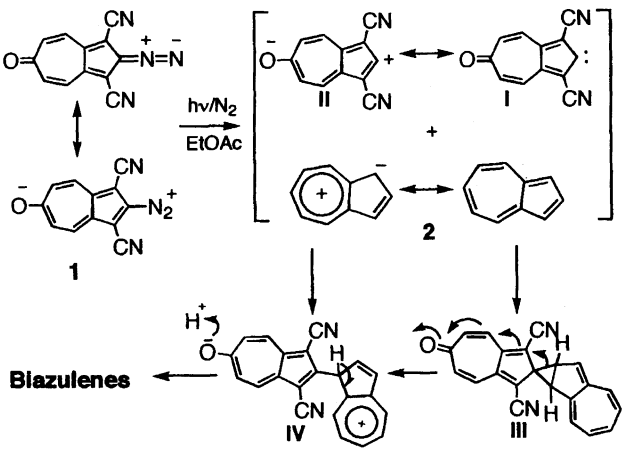
Since azulenes are highly polarized hydrocarbons, the photolysis of **1** in azulenes may also cause the arylation, from which the major products are expected to be 1,2′-biazulene derivatives. Indeed, this was the case. Herein we want to show the nearly quantitative preparation in a single-step operation to provide a new method of synthesis.

Thus, the photolysis of 2-diazo-1,3-dicyanoazulen-6(2*H*)-one (**1**, DAQ)[11] with several azulenes, i.e., **2a** = azulene, **2b** = 4,6,8-trimethylazulene, **2c** = 7-isopropyl-1,4-dimethylazulene (guaiazulene); **2d** = 2-methoxyazulene, and **2e** = 2-(acetylamino)azulene, always gave, together with 1,3-dicyanoazulen-6-ol (**3**), 2-(1-azulenyl)-1,3-dicyanoazulen-6-ols (1,2′-biazulenes, **4**) and 2-(5-azulenyl)-1,3-dicyanoazulen-6-ols (2,5′-biazulenes, **5**), of which **4** was the major.

It is well understood that irradiation of **1** should yield the extended ketocarbene, whose structure should be expressed as the hybrid species of the singlet carbene **I** and the zwitterion **II** (Scheme 2). Its delocalized structure is favored



Scheme 1.



Scheme 2.

by electron-withdrawing groups in the molecule, i.e., 6-oxo group and 1,3-dicyano group, and this electronic reversal in the azulene system, the positive charge on the five-membered ring, where the electron density in usual azulenes is high, should make it quite reactive at the C-2 position toward nucleophiles.[12—14]

As a singlet carbene, **I** might form the spiro intermediates with azulenes, whilst as dipolar species, **II** should form a covalent bond to the electronegative site of the reactant azulenes. Thus, the photolysate should be expressed as an aryl cation, rather than the ketocarbene. From the either of the routes, regeneration of the fully conjugated system should result in the 1,2′-biazulene derivatives.

Photoreaction of 1 with Parent Azulene and Alkylazulenes. When **1** was photolyzed in ethyl acetate solution in the presence of an equimolar amount of parent azulene (**2a**), two products (**3** and **4a**) were obtained. The byproduct **3** was a common product in this series of reactions,[11,12] and it must not be a biazulene derivative; the NMR spectroscopy led to formulate it as 1,3-dicyanoazulen-6-ol as shown in Scheme 3.

The major product (**4a**), formed in 92% yield, was deduced from the NMR spectroscopy; it retained a symmetrical 1,3-dicyanoazulene moiety from the A_2B_2-type doublet of doublets at $\delta = 6.58$ and 7.59 (2H each, $J = 12.4$, 1.5 Hz) and it showed a triplet signal at 7.80 (t, $J = 10.1$ Hz) to eliminate possibilities for 2,5′- and 2,6′-biazulene structures. A possibility of 2,4′- (or 2,8′-) structure was also eliminated by doublet signals with large magnitude of *vis*-couplings at 8.42 (d, $J = 9.1$ Hz) and 9.39 (d, $J = 9.9$ Hz). Therefore, **4a** is 2-(1-azulenyl)-1,3-dicyanoazulen-6-ol. The ^{13}C NMR spectrum, showing seventeen separated signals, is consistent with this formulation.

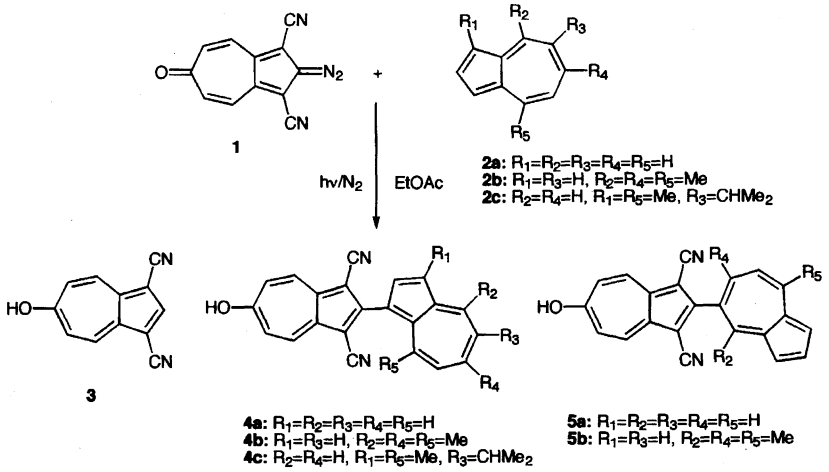
The minor product (**5a**), in 0.5% yield, showing also seventeen signals, was identified to be 2-(5-azulenyl)-1,3-dicyanoazulen-6-ol.

As an alkylazulene, 4,6,8-trimethylazulene (**2b**) also afforded two biazulenes (**4b** and **5b**) together with **3**; both biazulenes **4b** and **5b** showed three singlet methyl signals in ^{1}H NMR spectra, at 2.52, 2.71, and 3.19 (**4b**) and 2.59, 3.86, and 3.44 (**5b**) to rule out the diazulenylmethane structures. The major product, **4b**, in 87% yield, was 1,3-dicyano-2-(4,6,8-trimethyl-1-azulenyl)azulen-6-ol from the two singlet signals observed at 6.36 and 6.42 ascribable to the proton signals of the seven-membered ring (C-5 and C-7 positions). The minor product **5b**, 6% yield, was 1,3-dicyano-2-(4,6,8-trimethyl-5-azulenyl)azulen-6-ol from the three proton signals on the five-membered ring at 6.78 (dd, $J = 4.1$, 3.9 Hz), 7.14 (d, $J = 3.9$ Hz), and 8.18 (d, $J = 4.1$ Hz).

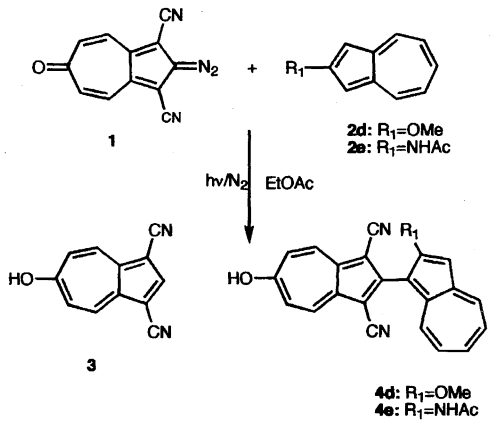
Guaiazulene, 7-isopropyl-1,4-dimethylazulene (**2c**), instead gave a single biazulene, 1,3-dicyano-2-(7-isopropyl-1,4-dimethyl-3-azulenyl)azulen-6-ol (**4c**). Again, a possibility of diazulenylmethane structure for **4c** was ruled out by observing all alkyl signals intact, at 1.29 (6H, d, $J = 4.4$ Hz), 2.60 (3H, s), and 3.38 (3H, s). In addition, an appearance of a singlet signal at 8.16, which should be ascribable to C-2 proton, and the presence of two protons in a vic-positions, at 7.26 (d, $J = 11.1$ Hz) and 7.86 (dd, $J = 11.0$, 2.2 Hz), identified the structure of **4c** to be as depicted. The failure to detect a 2,5′-biazulene derivative in this case should not be due to a steric hindrance, since **5b** was obtained from a more hindered precursor.

Photoreaction of 1 with 2-Methoxy- and 2-(Acetylamino)azulenes. Other than alkylazulenes, we have extended the study to that with derivatives carrying characteristic groups. Thus easily available 2-methoxyazulene (**2d**) gave a single product (**4d**) in 91% yield (Scheme 4). Its ^{1}H and ^{13}C NMR spectra clearly showed to be 1,3-dicyano-2-(2-methoxy-1-azulenyl)azulen-6-ol; it showed eighteen separated signals in ^{13}C NMR spectrum, one additional methoxy carbon signal to seventeen signals in **4a**, with a good correlation in chemical shifts and a singlet signal at 7.03 ascribable to C-3 proton in the ^{1}H NMR spectrum.

Also, 2-(acetylamino)azulene (**2e**) gave a single product (**4e**) in 89% yield. Its structure, 2-(2-acetylamino-1-azulenyl)-1,3-dicyanoazulen-6-ol, was deduced similarly from the NMR spectroscopy; it revealed nineteen signals in ^{13}C NMR and a singlet signal at 8.08, ascribable to C-3



Scheme 3.



Scheme 4.

proton, in ^{1}H NMR spectra.

Discussions. After all, the photolysis of **1** was very neat and clean, and the results were satisfactory from a synthetic viewpoint, i.e., besides the simple operations required and high yields for all the azulenes examined, it is easily handled in large quantities. A stoichiometric amount of azulene derivatives to **1** was satisfactory to give excellent to nearly a quantitative yield of biazulenes, and this might indicate a pre-association of two components prior to photogeneration of the carbene. This is reasonable in view of the highly polarized electron structure of **1** as well as of azulenes (Scheme 2).

There has been no diazulenylmethane-type product from an alkylazulene, **2b** or **2c**. The higher site selectivity of the reaction is also attributable to the more polarized electronic structure of azulenes than that of benzene derivatives; e.g., with toluene and xylenes, **1** afforded biaryl methane derivatives along with the biaryl derivatives.[11,13] The difference might be attributable to the electronic contribution; the reactivity of an aryl cation, **II**, generated in aprotic solvent by photolysis, is more facilitated over that of a neutral ketocarbene **I**. In other words, **II** should be an extreme case of a delocalized ketocarbene to be stabilized as an aryl cation, and as a result, the C–H insertion process to form the diazulenylmethanes was totally diminished. The **II** would be a good model compound for unsolvated aryl cation species.

Accompanied formations of 2,5′-biazulenes are explained well with the frontier electron theory; beside the highest electron density for C-5 or C-7 among the seven-membered ring carbons of azulene, the HOMO coefficient of C-5 or C-7, being next to the largest value of C-1 or C-3, i.e., +0.5456 (C-1), 0 (C-2), −0.5456 (C-3), −0.2586 (C-3a), +0.1103 (C-4), +0.3327 (C-5), 0 (C-6), −0.3327 (C-7), −0.1103 (C-8), and +0.2586 (C-8a) predicts the reactivity.[15] In cases of **2c**, **2d**, and **2e**, the absence of 2,5′-biazulene derivatives is, not due to the steric factor, but due to an enhanced reactivity of C-1 position by the mesomeric effect of the substituents on C-2 position, since **2b** did afford a 2,5′-biazulene derivative, **5b**. The observed predominance of 1,2′-biazulenes is interpretable in terms of significance of the structure **II** over **I**.[16]

In conclusion, the present procedure established a way to obtain 1,2′-biazulenes.

Experimental

The NMR spectra were measured by means of Brucker AC 300 Model spectrometers in acetone-d_6 at 300 MHz for protons and 75 MHz for carbons; the chemical shifts are expressed in δ units. The mass spectra were measured with a Finnigan TSQ-46-C spectrometer. The IR spectra were taken as KBr disks, using a Perkin–Elmer 983 G spectrometer. The UV-vis spectra were taken with a Shimadzu UV-3101 PC MODEL spectrophotometer in methanol solutions. The stationary phase for column chromatography was Merck 7734 (70—230 mesh).

Photolysis of 1 with 2a. An anhydrous EtOAc solution (400 cm^3) of **1** (100 mg, 0.455 mmol) and **2a** (63 mg, 0.492 mmol) was sealed in two Pyrex glass tube (4 cm×40 cm) after degassing (replacement by N_2 gas) and irradiated in a Rayonet Irradiator (RPR-100) equipped with 16 RPR 3000 A lamps and a bottom fan for 1.5 h. The solvent was evaporated in vacuo and the residue was chromatographed on a silica-gel column by using EtOAc and recrystallized from acetone to give **4a** [violet needles, mp > 300 °C, 134 mg, 92%. Found: *m/z* 320.3497 (M$^+$). Calcd for $C_{22}H_{12}N_2O$: M, 320.3500. ^{1}H NMR δ = 6.58 (2H, dd, 12.4, 1.5 Hz), 7.33—7.51 (3H, m), 7.59 (2H, dd, J = 12.4, 1.5 Hz), 7.80 (1H, t, J = 10.1 Hz), 8.29 (1H, d, J = 4.7 Hz), 8.42 (1H, d, J = 9.1 Hz), and 9.39 (1H, J = d, 9.9 Hz); ^{13}C NMR δ = 88.0 (2C), 119.0 (2C), 121.2, 124.7, 126.8, 127.2, 127.4, 128.6 (2C), 130.0 (2C), 133.4 (2C), 136.5, 136.8, 137.2, 139.4, 140.8, 144.8, and 183.5; UV-vis λ_{max} = 325 nm (log ε = 3.53), 376 (3.15), 525 (3.46), and 553 (3.44); IR ν = 2200 and 1587 cm^{-1}; MS(FAB) *m/z* 321 (M+1$^+$; 11), 193 (56), and 139 (82)], **5a** [violet needles, mp > 300 °C, 7 mg, 5%. Found: *m/z* 320.3496 (M$^+$). Calcd for $C_{22}H_{12}N_2O$: M, 320.3500. ^{1}H NMR δ = 6.79 (1H, d, J = 2.0 Hz), 7.16 (1H, d, J = 2.0 Hz), 7.43—7.52 (5H, m), 8.30 (1H, d, J = 4.5 Hz), 7.83 (1H, t, J = 9.6 Hz), 8.46 (1H, d, J = 9.6 Hz), and 9.44 (1H, d, J = 9.6 Hz); ^{13}C NMR δ = 88.2 (2C), 118.3 (2C), 121.4, 122.0, 124.8, 125.2, 127.6$_6$, 127.7$_3$ (2C), 131.7 (2C), 132.0 (2C), 136.1, 136.4, 137.4, 139.3, 140.9, 143.4, and 183.0; UV-vis λ_{max} = 329 nm (log ε = 3.38), 404 (2.91), 535 (3.51), and 571 (3.46); IR ν = 2934, 2200, and 1593 cm^{-1}; MS (FAB) *m/z* 321 (M+1$^+$; 7), 193 (53), 139(83), and 107 (100)], and **3** (yellow needles, 1 mg, 1%) which was identical with the previously obtained authentic sample.[11,12]

Photolysis of 1 with 2b. Similar to the above, an anhydrous EtOAc solution (400 cm^3) of **1** (100 mg) and **2b** (84 mg, 0.494 mmol), sealed in two Pyrex glass tubes (4 cm×40 cm), was irradiated in a Rayonet Irradiator (RPR-100) for 1.5 h. The solvent was evaporated in vacuo and the residue was chromatographed on a silica-gel column by using EtOAc and recrystallized from acetone to give **4b** [violet needles, mp > 300 °C, 143 mg, 87%. Found: *m/z* 362.4303 (M$^+$). Calcd for $C_{25}H_{18}N_2O$: M, 362.4307. ^{1}H NMR δ = 2.52 (3H, s), 2.71 (3H, s), 3.19 (3H, s), 5.81 (2H, dd, J = 9.8, 1.3 Hz), 6.36 (1H, s), 6.42 (1H, s), 6.49 (1H, d, J = 4.1 Hz), 6.65 (2H, dd, J = 9.8, 1.3 Hz), and 7.14 (1H, d, J = 4.1 Hz); ^{13}C NMR δ = 24.8, 27.8, 29.1, 86.7 (2C), 117.9 (2C), 118.3, 121.8, 124.3, 129.5 (2C), 130.7, 131.7, 132.1 (2C), 132.4 (2C), 137.4, 140.0, 147.4, 147.9, 148.6, 150.0, and 186.4; UV-vis λ_{max} = 329 nm (log ε = 3.27), 421 (2.75), and 559 (3.28); IR ν = 2934, 2200, and 1579 cm^{-1}; MS (FAB) *m/z* 362 (M$^+$; 11), 339 (17), 287 (95), 285 (100), and 271 (39)], **5b** [violet needles, mp > 300 °C, 10 mg, 6%. Found: *m/z* 362.4306 (M$^+$). Calcd for $C_{25}H_{18}N_2O$: M, 362.4307. ^{1}H NMR δ = 2.59 (3H, s), 2.86 (3H, s), 3.44 (3H, s), 6.78 (1H, dd, J = 4.1, 3.9 Hz), 7.14 (1H, d, J = 3.9 Hz), 7.27 (1H, s), 7.36—7.43 (4H, m), and 8.18 (1H, d, J = 4.1 Hz); ^{13}C NMR δ = 23.6, 24.5, 25.2, 88.6

(2C), 117.4, 118.6 (2C), 123.2, 126.5, 129.6 (2C), 130.0, 130.9, 132.1 (2C), 132.8 (2C), 137.6, 141.1, 147.7, 148.9, 149.6, 151.3, and 188.0; UV-vis λ_{max} = 324 nm (log ε = 3.24), 405 (2.81), and 553 (3.26); IR ν = 2927, 2853, 2200, 1625, and 1580 cm^{-1}; MS (FAB) *m/z* 362 (M^+; 10), 339 (17), 287 (96), 285 (100), and 271 (38), and **3** (2 mg, 2%).

Photolysis of 1 with 2c. An anhydrous EtOAc solution (400 cm^3) of **1** (100 mg) and **2c** (98 mg, 0.495 mmol) was similarly irradiated in a Rayonet Irradiator (RPR-100) for 1.5 h. The solvent was evaporated in vacuo and the residue was chromatographed on a silica-gel column by using EtOAc and recrystallized from acetone to give the products, **4c** [violet needles, mp > 300 °C, 155 mg, 87%. Found: *m/z* 390.4842 (M^+). Calcd for $C_{27}H_{22}N_2O$: M, 390.4844. ^{1}H NMR δ = 1.29 (6H, d, *J* = 4.4 Hz), 2.60 (3H, s), 2.73 (1H, sept, *J* = 4.4 Hz), 3.38 (3H, s), 6.55 (2H, dd, *J* = 12.3, 2.5 Hz), 7.26 (1H, d, *J* = 11.1 Hz), 7.55 (2H, dd, *J* = 12.3, 2.5 Hz), 7.86 (1H, dd, *J* = 11.1, 2.2 Hz), 8.16 (1H, s), and 8.63 (1H, d, *J* = 2.2 Hz); ^{13}C NMR δ = 12.9 (2C), 25.2, 28.2, 32.1, 86.7 (2C), 118.0 (2C), 125.0, 128.3, 129.0 (2C), 129.5, 130.7, 131.8$_7$ (2C), 131.9$_2$ (2C), 132.2, 133.3, 134.9, 141.6, 145.6, 146.9, 149.5, and 186.5; UV-vis λ_{max} = 329 nm (log ε = 3.50), 429 (3.11), 531 (3.65), and 588 (3.66); IR ν = 2934, 2362, 2200, and 1640 cm^{-1}; MS(FAB) *m/z* 391 ($M+1^+$; 30), 289 (7), 176 (20), 154 (65), 149 (100), and 136 (52)] and **3** (4 mg, 5%). Detection of other products failed as regards NMR spectroscopy.

Photolysis of 1 with 2d. Similar to the above, an anhydrous EtOAc solution (400 cm^3) of **1** (100 mg) and **2d** (78 mg, 0.494 mmol) was irradiated in a Rayonet Irradiator (RPR-100) for 1.5 h. The solvent was evaporated in vacuo and the residue was chromatographed on a silica-gel column by using EtOAc and recrystallized from acetone to give **4d** [violet needles, mp > 300 °C, 145 mg, 91%. Found: *m/z* 350.3767 (M^+). Calcd for $C_{23}H_{14}N_2O_2$: M, 350.3763. ^{1}H NMR δ = 4.13 (3H, s), 6.60 (2H, d, *J* = 11.8 Hz), 7.03 (1H, s), 7.36—7.48 (3H, m), 7.61 (2H, d, *J* = 11.8 Hz), 8.19 (1H, d, *J* = 9.8 Hz), and 9.41 (1H, d, *J* = 9.3 Hz); ^{13}C NMR δ = 60.1, 88.2 (2C), 119.1 (2C), 119.5, 123.7, 124.7, 129.0 (2C), 132.1 (2C), 134.1 (2C), 135.3, 135.4, 137.0, 141.1, 148.5, 149.8, 151.9, 170.4, and 180.3; UV-vis λ_{max} = 323 nm (log ε = 3.47), 371 (3.26), 418 (3.00), and 541 (3.49); IR ν = 2934, 2200, and 1579 cm^{-1}; MS (FAB) *m/z* 351 ($M+1^+$; 11), 279 (42), 207 (40), 167 (70), and 149 (100)] and **3** (3.5 mg, 4%).

Phtolysis of 1 with 2e. Similar to the above, an anhydrous EtOAc solution (400 cm^3) of **1** (100 mg) and **2e** (86 mg, 0.465 mmol) was irradiated in a Rayonet Irradiator (RPR-100) for 1.5 h. The solvent was evaporated in vacuo and the residue was chromatographed on a silica-gel column by using EtOAc and recrystallized from acetone to give **4e** [violet needlds, mp > 300 °C, 155 mg, 89%. Found: *m/z* 377.1166 (M^+). Calcd for $C_{24}H_{15}N_3O_2$: M, 377.1164. ^{1}H NMR δ = 2.36 (3H, s), 6.59 (2H, dd, *J* = 11.7, 1.5 Hz), 7.44—7.51 (2H, m), 7.57 (2H, dd, *J* = 11.7, 1.5 Hz), 7.70 (1H, t, *J* = 9.8 Hz), 8.08 (1H, s), 8.29 (1H, d, *J* = 9.4 Hz), and 9.19 (1H, d, *J* = 9.5 Hz); ^{13}C NMR δ = 24.6, 87.0 (2C), 108.2, 118.2 (2C), 124.5, 128.8, 129.3, 129.8 (2C), 131.6 (2C), 132.5 (2C), 136.2, 136.3, 137.3, 138.0, 140.4, 143.5, 147.8, 169.4, and 186.5; UV-vis λ_{max} = 324 nm (log ε = 3.43), 371 (3.15), 441 (2.68), and 547 (3.08); IR ν = 3471, 2978, 2205, 1680, and 1541 cm^{-1}; MS (FAB) *m/z* 378 ($M+1^+$; 2), 176 (42), 154 (91), and 136 (100)] and **3** (4 mg, 5%).

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15) The HOMO coefficients of parent azulene were calculated by CAChe ExtHückel application (CaChe System version 3.7, CaChe Scientific Inc.) using CaChe Extended Hückel parameters with its default setting (STO-3G basis set and 1.75 for Wolfberg–Helmholtz constant) for the preserved structure of azulene in the 'Fragment Library'. cf., R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); G. D. Purvis, *J. Comp. Aided Mol. Des.*, **5**, 55 (1991).

16) A referee raised a question, i.e., if one considers a involvement of resonance hybrid **I** in the reaction, why **III** should give **4** exclusively? One should provide an explanation for an absence of 2,2′-biazulenes among the products. Indeed, we agree that **II** is more important than **I**, but it is not appropriate to totally ignore the contribution of **I**. The **1** is shown to give various C–H insertion products with various compounds. The absence of 2,2′-biazulene should be explained as the instability of intermediate **IV′** being equivalent to the C-2 protonated species of an azulene derivative. (Chart 1. Structure **IV′**).

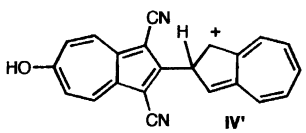

Chart 1. Structure IV′.