A Convenient New Synthetic Route to Substituted Benz[*a*]azulenes

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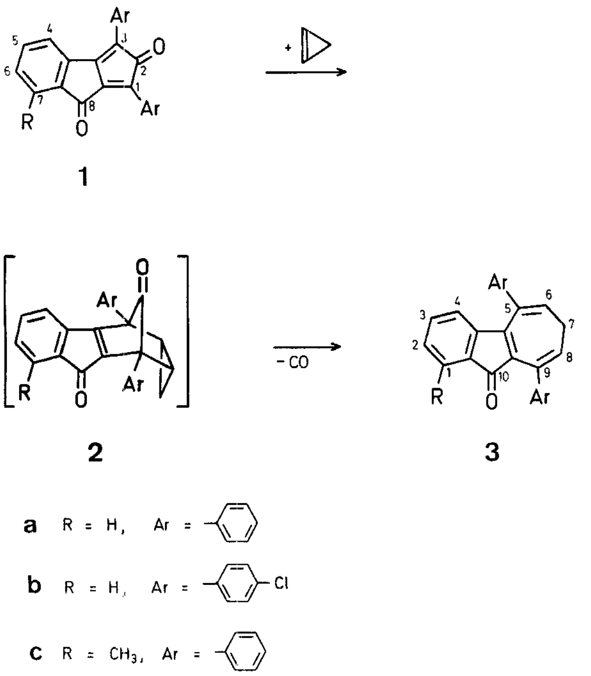
The Diels-Alder addition of substituted cyclopropenes to polysubstituted cyclopentadienones has provided a useful synthetic route to polysubstituted tropilidenes[1,2]. This method has also been used to advantage in the synthesis of polycyclic hydrocarbons containing a fused seven-membered ring[3].

In this paper, we report a further extension of this general method to provide a new entry into the benz[*a*]azulene system. Due to considerable flexibility in the synthetic scheme, a variety of substituted benz[*a*]azulenes now becomes available in good yield.



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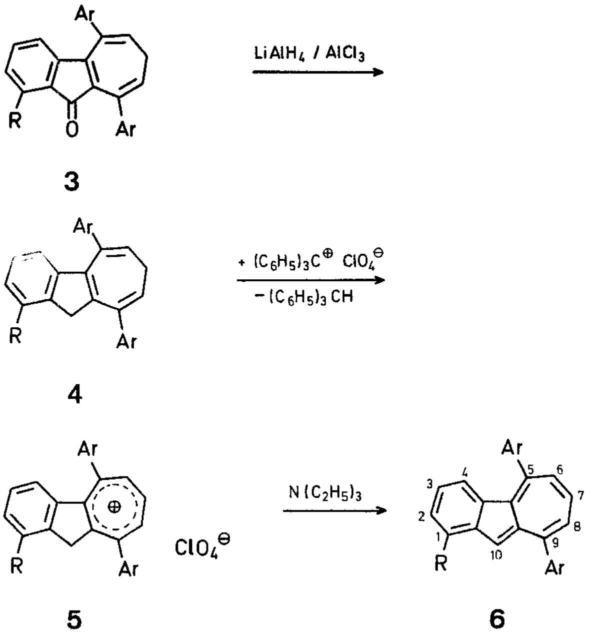
Cyclopropene, generated by the method of Closs and Krantz[4], was passed into a dichloromethane solution of the "indanocyclones" **1a–c**[5] at room temperature. The initial Diels-Alder adducts **2a–c** could not be isolated and apparently decarbonylate spontaneously under the reaction conditions to yield the 5,9-diaryl-10-oxo-7,10-dihydrobenz[*a*]azulenes **3a–c**. The conversions of the "indanocyclones" to the compounds **3a–c** were essentially quantitative.

Reduction of compounds **3a–c** directly to the hydrocarbons **4a–c** was accomplished by means of lithium aluminum hydride/anhydrous aluminum chloride in refluxing ether. The yields in this reduction were variable, but always in excess of 50%. Hydride abstraction with trityl perchlorate in dry dichloromethane converted the hydrocarbons **4a–c** to the unstable benz[*a*]azulenium cations **5a–c**. In the case of **5a**, the cation could be isolated; however, further purification was unsuccessful as the species was very prone to deprotonate even in ether solution to the benz[*a*]azulenes **6a–c**. Nevertheless, sufficient spectral data (I.R. and N.M.R.) were obtained on cations **5a–c** to support the proposed structures.



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The benz[*a*]azulenium cations **5a–c** were readily converted to the benz[*a*]azulenes **6a–c** in essentially quantitative yield by treatment with triethylamine in dichloromethane solution. Benz[*a*]azulenes **6a–c** form beautiful blue-black crystals, and are intensily blue in solution (refer to Table 1).

"Indanocyclones" 1a–c:

Compounds **1a–c** were synthesized according to the method of Ried and Freitag[5]. In the case of **1b** (m.p. 285–286°), the 1,3-bis-[4-chlorophenyl]-2-propanone was synthesized by the method of Becker et al.[6]. The 3-methylninhydrin (m.p. 126–127°) required in the synthesis of **1c** (m.p. 243–244°) was prepared using the procedure of Russell and Becker[7]. It is interesting to note that in the condensation of the 3-methylninhydrin with 1,3-diphenylacetone only one of the two possible "indanocyclones" is formed. This is presumably a consequence of steric control.

Table 1. Product Data for 5,9-Diarylbenz[*a*]azulenes **6a–c**

Compound	Yield[a] %	m.p.	Analysis	U.V. $\lambda_{max}(\log\varepsilon)$[d]	Mol. Weight[e]
6a	79	136–137°[b]	calc. C 94.51 H 5.49 found 94.24 5.37	617 (2.74)	330
6b	52	178–179°[c]	calc. C 78.20 H 4.04 found 78.10 4.18	620 (2.75)	398
6c	51	171–172°[c]	calc. C 94.15 H 5.85 found 93.86 5.93	625 (2.74)	344

[a] based on **4a–c** [b] from ethanol [c] from benzene/ligroin [d] in cyclohexane [e] by mass spectrometry

Table 2. Product Data for 5,9-Diaryl-7,10-dihydrobenz[*a*]azulenes **3** and **4**

Compound	Yield %	m.p.	Analysis	Mol. Weight[a]
3a	100	180–181°[b]	calc. C 90.14 H 5.24 found 90.23 5.32	346
3b	100	221–222°[b]	calc. C 75.19 H 3.88 found 74.91 3.93	414
3c	100	199–200°[b]	calc. C 89.97 H 5.59 found 90.17 5.47	360
4a	79	[c]	calc. C 93.94 H 6.06 found 93.74 6.17	332
4b	71	[c]	calc. C 77.81 H 4.52 found 77.87 4.77	400
4c	58	[c]	calc. C 93.60 H 6.40 found 93.33 6.47	346

[a] by mass spectrometry
[b] from ethanol
[c] non-crystalline glass

5,9-Diaryl-10-oxo-7,10-dihydrobenz[*a*]azulenes 3a–c:

Cyclopropene was generated by the method of Closs and Krantz[4] and bubbled into a dichloromethane solution of the "indanocyclones" **1a–c** until their characteristic purple color was discharged. The solutions were orange to red-orange upon completion of the reaction. The solvent was then removed and the residue was recrystallized from 95% ethanol to yield the yellow-orange crystalline ketones **3a–c** (see Table 2).

5,9-Diaryl-7,10-dihydrobenz[*a*]azulenes 4a–c:

5,9-Diaryl-10-oxo-7,10-dihydrobenz[*a*]azulene **3a–c** (1 mmol) was suspended (dissolved) in anhydrous diethyl ether (25 ml). To this was added anhydrous aluminum chloride (2 mmol) followed by lithium aluminum hydride (2 mmol). The reaction mixture was refluxed for 2 hr, cooled, and quenched with ammonium chloride solution. The organic layer was separated, washed several times with water, and dried over anhydrous magnesium sulfate. Removal of solvent left a residue which on chromatography on alumina (50% benzene/hexane) afforded the desired hydrocarbons **4a–c** as glassy solids.

5,9-Diarylbenz[*a*]azulenium Perchlorates 5a–c:

Hydrocarbon **4a–c** (1 mmol) and an equivalent amount of freshly prepared trityl perchlorate[8] were dissolved with magnetic stirring in dry dichloromethane (3 ml). Stirring was continued for 1 hr at room temperature. In the case of **5a**, the cation precipitated out of solution, whereas with **5b** and **5c** it was necessary to carefully precipitate the cation from solution with a minimal volume of hexane. The perchlorates **5a–c** were quickly filtered, washed several times with hexane, and vacuum-dried. Recrystallization of the perchlorates was not successful. The N.M.R. (60 MHz) of **5a** displayed an unsymmetrical 3H multiplet centered at $\tau = 1.25$–1.30, and a 2 H singlet at $\tau = 5.52$ along with the expected aromatic protons (14 H) appearing as a multiplet at $\tau = 2.30$–3.22.

5,9-Diarylbenz[*a*]azulenes 6a–c:

To the 5,9-diarylbenz[*a*]azulenium perchlorate **5a–c** (1 mmol) dissolved in dichloromethane (10 ml), a solution of triethylamine (1 mmol) in dichloromethane (5 ml) was added whereupon the deep blue color of the 5,9-diarylbenz[*a*]azulene appeared. The reaction mixture was filtered and the solvent removed. The residue was chromatographed on alumina with 10–25% benzene/hexane eluting the desired compound **6a–c** (see Table 1). The N.M.R. spectra of the 5,9-diarylbenz[*a*]azulenes **6a–c** exhibited complex signals for the aromatic protons appearing at $\tau = 2.2$–3.6. Compound **6c** showed a 3 H singlet at $\tau = 7.50$.

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[1] M.A. Battiste, Chem. & Ind. **1961**, 550.
[2] M.A. Battiste, T. J. Barton, Tetrahedron Letters **1968**, 2951.
[3] M.A. Battiste, J. Amer. Chem. Soc. **85**, 2175 (1963).
[4] G.L. Closs, K.D. Krantz, J. Org. Chem. **31**, 638 (1966).
[5] W. Ried, D. Freitag, Chem. Ber. **99**, 2675 (1966).
[6] F.J. Thaller, D.E. Trucker, E.I. Becker, J. Amer. Chem. Soc. 73, 228 (1951).
[7] H.D. Becker, G.A. Russell, J. Org. Chem. **28**, 1896 (1963).
[8] H. J. Dauben, L. R. Honnen, K. M. Harmon, J. Org. Chem. **25**, 1442 (1960).