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# Diels–Alder approach to the synthesis of azulene-substituted benzene derivatives. Synthesis and redox behavior of 1,2-di(6-azulenyl)tetraphenylbenzenes

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## Abstract

1,2-Di(6-azulenyl)tetraphenylbenzenes and (6-azulenyl)pentaphenylbenzenes were synthesized by Diels–Alder reaction of di(6-azulenyl)acetylenes and 6-(phenylethynyl)azulenes with tetraphenylcyclopentadienone. Mono(6-azulenyl)benzenes exhibited a reduction wave upon cyclic voltammetry (CV). In contrast to the benzene derivatives, di(6-azulenyl)benzenes showed a two-step reduction wave at similar potential region upon CV, which revealed the formation of dianions stabilized by 6-azulenyl substituents under electrochemical reduction conditions. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* ethynylazulenes; Pd-cross-coupling reaction; Diels–Alder reaction; azulenylbenzenes.

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Azulene ($C_{10}H_8$) is a theoretically interesting compound with many unusual properties.[1] Especially, the azulene system has a tendency to stabilize cations, as well as anions owing to its remarkable polarized properties, which are utilized to construct extremely stable methyl cations.[2] Recently, much attention has been focused on the aromatic compounds with extended π-electron systems because of their special optical and electrical properties.[3] However, to date, molecules with potentially useful electronic properties constructed by non-benzenoid aromatic compounds are fairly scarce. We have recently developed a simple route to unknown 1,3,5-tri(1-azulenyl)benzenes by tetrachlorosilane-mediated cyclotrimerization of 1-acethylazulenes.[4] Very recently, Hafner et al. reported the ethynylation of azulenes in a five-membered ring utilizing Pd-catalyzed cross-coupling reaction of bromo- and iodoazulenes with trimethylsiliylacetylene[5] and the cyclooligomerization of the 1-ethynylazulenes catalyzed by $CpCo(CO)_2$ to afford 1-azulenylbenzene derivatives and (cyclobutadiene)cobalt complexes in low yields.[6]

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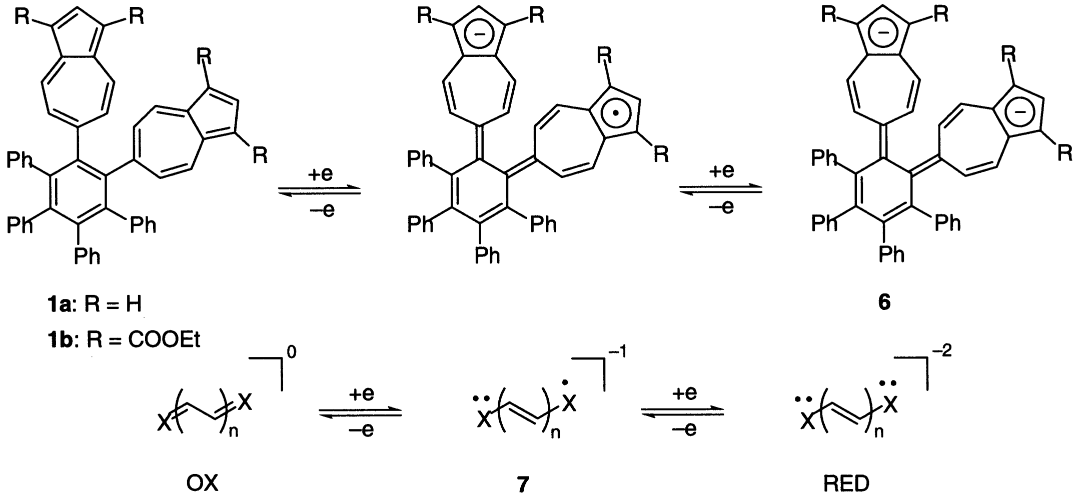
Herein we report an efficient preparation of azulene-substituted benzene derivatives by Diels–Alder reaction of di(6-azulenyl)acetylenes (**3a** and **3b**) and 6-(phenylethynyl)azulenes (**4a** and **4b**) with tetraphenylcyclopentadienone (**5**) to afford novel 6-azulenylbenzene derivatives **1a**, **1b**, **2a**, and **2b**, which are expected to have a different character from that of 1-azulenylbenzene derivatives.[7] According to the nature of the azulene systems, **1a** and **1b** would exhibit the formation of stabilized closed shell dianions **6** by electrochemical reduction (Scheme 1). Although there are many reports concerning carbocations stabilized by 1-azulenyl substituents, little is known about carbanions stabilized by 6-azulenyl substituents because of the synthetic difficulty of the functionalization of azulene in a seven-membered ring.[1] Thus, we also report here the redox behavior of these novel 6-azulenylbenzene derivatives (**1a**, **1b**, **2a**, and **2b**) and 6-azulenylacetylenes (**3a**, **3b**, **4a**, and **4b**) examined by cyclic voltammetry (CV).



**1a**: R = H
**1b**: R = COOEt

**6**

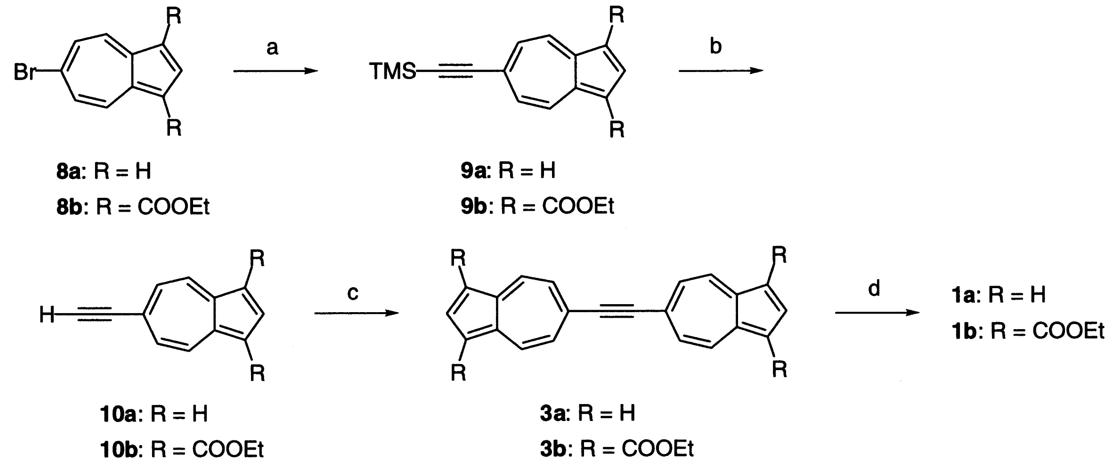
OX

**7**

RED

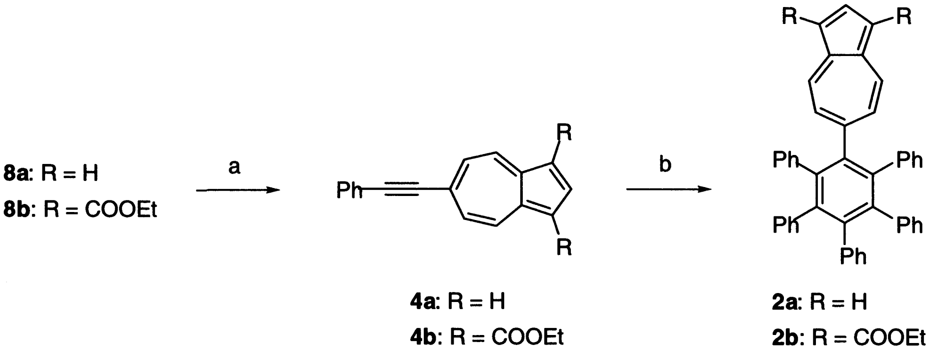
Scheme 1. Redox system for the reduction of **1a**, **1b** and that for a general structure of violenes **7**

Pd-catalyzed cross-coupling reaction of 6-bromoazulenes (**8a** and **8b**)[8] with trimethylsilylacetylene under Sonogashira–Hagihara conditions[9] at room temperature afforded 6-(trimethylsilylethynyl)azulenes (**9a** and **9b**) in 86 and 84% yields, respectively. It is noteworthy that the ethynylation of azulenes in the seven-membered ring readily proceeded using bromides at room temperature. Treatment of **9a** and **9b** with potassium fluoride in DMF furnished 6-ethynylazulenes (**10a** and **10b**)[10] in 78 and 93% yields, respectively. Cross-coupling reaction of **10a** with **8a** using $PdCl_2(PPh_3)_2$ as a catalyst afforded an inseparable mixture (1:2.2) of di(6-azulenyl)acetylene (**3a**) and di(6-azulenyl)diacetylene (**11**), which was obtained from the oxidative coupling of **10a** by the Pd-catalyst.[9,11] However, we found that the reaction of **10a** with **8a** utilizing $Pd(PPh_3)_4$ as a catalyst exclusively gave the desired **3a** in 98% yield. Similarly, **3b** was obtained by the reaction of **10b** with **8b** under similar conditions in 96% yield. Diels–Alder reaction of **3a** and **3b** with a large excess of **5** in diphenyl ether at 160°C under an Ar atmosphere for 1–2 days and subsequent chromatographic purification of the reaction mixture on silica gel afforded **1a** and **1b** in 13 and 91% yields, respectively (Scheme 2).[12]



Scheme 2. Synthesis of **1a** and **1b**. (a) TMSA, $[PdCl_2(PPh_3)_2]$, $PPh_3$, CuI, $Et_3N$, toluene, rt, 2.5 h (86%) for R=H, 1.5 h (84%) for R=COOEt; (b) KF, $H_2O$, DMF, rt, 3 h (78%) for R=H, 3 h (93%) for R=COOEt; (c) **8a** and **8b**, $[Pd(PPh_3)_4]$, $PPh_3$, CuI, $Et_3N$, toluene, rt, 3 h (98%) for R=H, 1.5 h (96%) for R=COOEt; (d) **5**, diphenyl ether, 160°C, 2 days (13%) for R=H, 1 day (91%) for R=COOEt

Synthesis of **2a** and **2b** as outlined in Scheme 3 also commenced with **8a** and **8b**, respectively. 6-(Phenylethynyl)azulenes (**4a** and **4b**) were prepared by the Sonogashira reaction of **8a** and **8b** with phenylacetylene in 90 and 87% yields, respectively. Diels–Alder reaction of **4a** and **4b** with a large excess of **5** in diphenyl ether at 140 and 160°C, respectively, under an Ar atmosphere for 5 days afforded **2a** and **2b** in 32 and 93% yields, respectively. The spectral features of **1a**, **1b**, **2a**, and **2b** are in agreement with the structure of these products. **1a**, **1b**, **2a**, and **2b** are remarkably stable, showing no decomposition even after several weeks at room temperature.



Scheme 3. Synthesis of **2a** and **2b**. (a) Phenylacetylene, $[PdCl_2(PPh_3)_2]$, $PPh_3$, CuI, $Et_3N$, toluene, rt, 5 h (90%) for R=H, 9 h (87%) for R=COOEt; (b) **5**, diphenyl ether, 160°C, 1 day (32%) for R=H, 140°C, 5 days (93%) for R=COOEt

1,2-Di(6-azulenyl)benzene **1b** exhibited the voltammogram, as shown in Fig. 1(a). The voltammogram was characterized by a barely separated two-step reduction wave at $E_{1/2}$ −1.57 and −1.72 V. **1a** also showed the transfer of two electrons at −2.00 and −2.20 V upon CV. Thus, the redox system of **1a** and **1b** is depicted to be like a general structure of violenes **7**, as shown

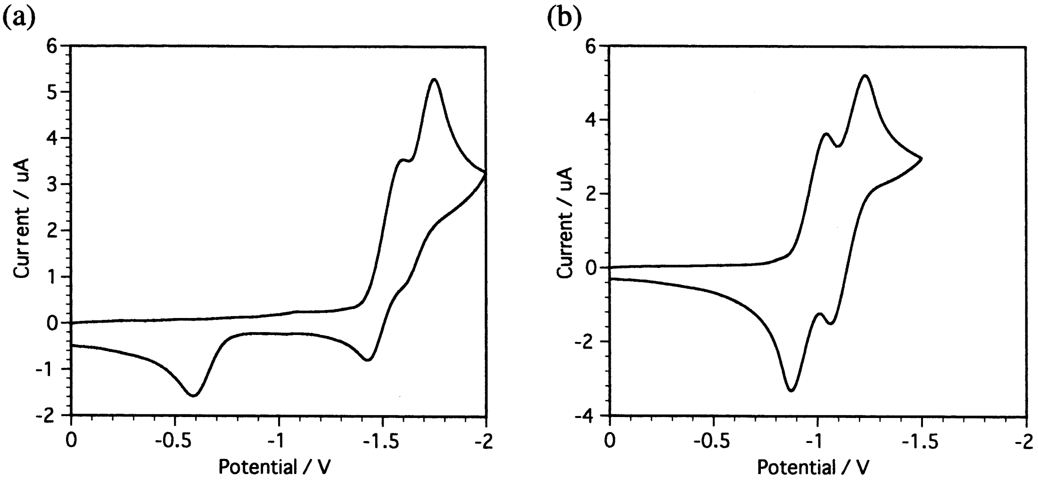
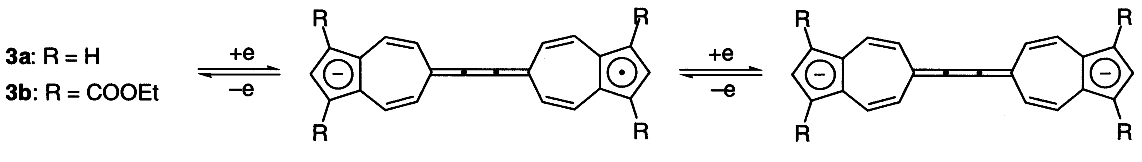


Figure 1. Cyclic voltammograms of (a) **1b** and (b) **3b** in THF containing $n$-$Bu_4N^+BF_4^-$ (0.1 M) as a supporting electrolyte; V versus Ag/$Ag^+$, Pt electrode, scan rate 100 mV $s^{-1}$, and Fc/$Fc^+$ = 0.10 V

in Scheme 1.[13] The less negative reduction potentials of **1b** compared with those of **1a** are attributable to the stabilization of anions by the ethoxycarbonyl groups substituted in the five-membered ring. The first reduction potentials and even the second ones of **1a** and **1b** are almost comparable with those of **2a** (−2.06 V) and **2b** (−1.63 V), respectively. Therefore, the two 6-azulenyl substituents on benzene in a 1,2 relationship increased its electron-accepting properties because of the closed-shell dianionic structure **6**. Unfortunately, the reduction waves of **1a** and **1b** showed poor reversibility, which exhibited the low stabilities of the expected radical anion and dianion **6** under the electrochemical reduction conditions. Thus, the measurement of the UV–vis spectroscopy of **1b** under electrochemical reduction conditions did not afford any evidence of the formation of the radical anion and/or dianion **7** due to the instability of these species.

1,2-Di(6-azulenyl)acetylenes **3a** and **3b** are also an example of the two-electron redox system stabilized by two 6-azulenyl substituents, as illustrated in Scheme 4. In contrast to the poor reversibility of **1a** and **1b**, **3a** and **3b** exhibited a reversible two-step reduction wave (**3a**, $E_{1/2}$ −1.41 and −1.61 V; **3b**, $E_{1/2}$ −0.96 and −1.15 V, respectively) upon CV (Fig. 1(b)). These reduction potentials of **3a** and **3b** are less negative than those of **4a** (−1.66 V) and **4b** (−1.29 V), respectively. Thus, the two 6-azulenyl substituents of **3a** and **3b** also increase the electron-accepting properties.



Scheme 4. Redox system for the reduction of **3a** and **3b**

We have demonstrated the Pd-catalyzed ethynylation of azulenes in a seven-membered ring using bromoazulenes and the efficient preparation of novel 6-azulenylbenzene derivatives **1** and **2**. Although the radical anion and dianion of **1** were not detected by UV–vis spectroscopy due to the instability of these species, **1** was clarified to represent the presumed two-step redox system upon CV. A cyclooligomerization approach to the synthesis of novel 6-azulenylbenzene derivatives using (6-azulenyl)acetylenes by transition metal-catalyzed reaction will be published elsewhere.

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