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Syntheses of mono-, di- and triethynylazulenes

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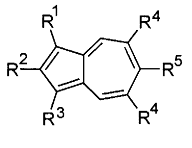
Abstract

Simple and productive routes to mono-, di- and triethynylazulenes are described. Azulenes ethynylated in the five-membered ring can be prepared on a multigram scale by Pd-catalyzed cross-coupling of iodo- or bromoazulenes with trimethylsilyl-acetylene and subsequent desilylation. 5,7-Diethynylazulene was synthesized by dibromomethylenation of the corresponding dialdehyde and subsequent dehydrobromination. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: ethynylazulenes; Pd-cross-coupling reaction; Corey–Fuchs reaction.

The increasing interest in aromatic compounds with extended π-electron systems because of their importance as materials with special optical and electrical properties for the design of molecular devices has focused in the last decades to a large extent on the synthesis of polyethynylated as well as donor and/or acceptor substituted benzenoid and heteroaromatic compounds.[1–3] However, up to now non-benzenoid aromatic or even antiaromatic π-electron systems were only scarcely employed as precursors for the synthesis of new materials with potential useful electronic properties. Especially, the azulene system with its pronounced polarizability and its tendency to form stabilized radical cations as well as anions should be predestinated as building block for the construction of new structures with interesting chemical and physical properties. With this respect we recently synthesized 2,4,6,8-tetracyanoazulene (TCNA) which proved to be a strong acceptor for electrically conductive charge-transfer complexes and radical anion salts.[4]

We report here on the synthesis of mono- and polyethynylated azulenes **1a**–**h** utilizing the now available versatile methods for new carbon–carbon bond forming reactions of modern acetylene chemistry[5] as well as the classical Corey–Fuchs reaction.[6]



1	a	b	c	d	e	f	g	h
R^1	≡	H	≡	≡	≡	≡	≡	H
R^2	H	≡	≡	H	≡	H	H	H
R^3	H	H	H	≡	≡	H	≡	H
R^4	H	H	H	H	H	H	H	≡
R^5	H	H	H	H	H	*t*-Bu	*t*-Bu	H

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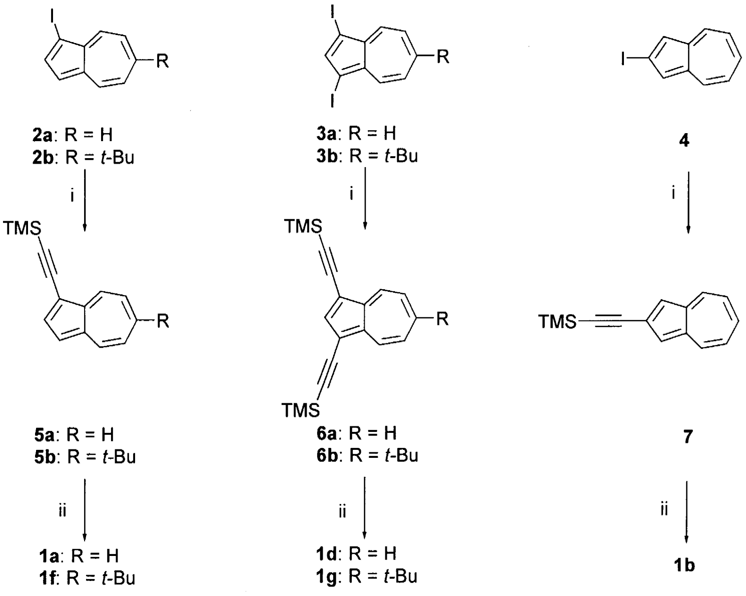
So far, only a few ethynylazulenes and some highly functionalized derivatives synthesized by multistep procedures with moderate yields were described.[7,8] In search of an expedient pathway to the azulenes **1a**–**g** ethynylated in the five-membered ring, our attentions focused on the alkynylation of the iodoazulenes **2**–**4**.[9] Thus, cross-coupling of **2**–**4** with trimethylsilyl-acetylene (TMSA) under Sonogashira–Hagihara conditions[10] afforded the trimethylsilyl-protected ethynylazulenes **5**–**7** in 80–90% yields as green or blue crystals.[11] Subsequent treatment of the (trimethylsilylethynyl)azulenes **5**–**7** with potassium hydroxide in methanol followed by chromatography on alumina (BII-III) using *n*-hexane as an eluent furnished blue crystals of the mono- and diethynylazulenes **1a**, **b**, **d**, **f** and **g**, respectively, in 90–100% yields (Scheme 1).

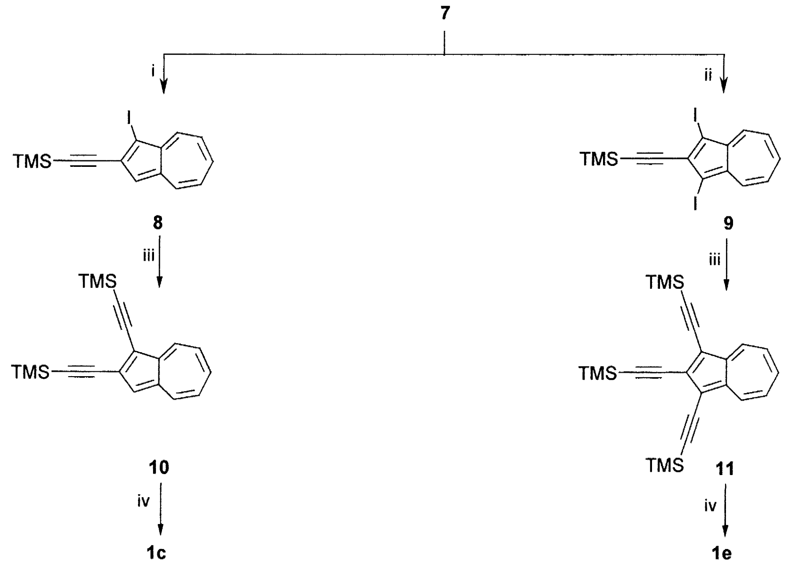


Scheme 1. (i) 0.04 mol% $PdCl_2(PPh_3)_2$, 0.08 mol% CuI, NEt_3, 1 or 2 equiv. TMSA, rt; (ii) 1.1 equiv. 1 M KOH in H_2O, MeOH, rt

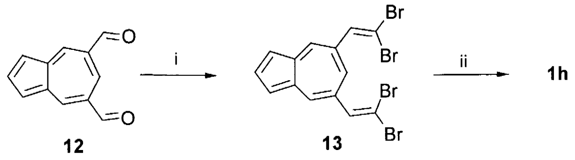
In analogy, the reaction of 2-(trimethylsilylethynyl)azulene (**7**) with one or two equivalents of *N*-iodosuccinimide leads to the formation of the corresponding mono- and diiodoazulenes **8** and **9**, respectively, which could be coupled with TMSA under Sonogashira conditions to give the 1,2-bis(trimethylsilylethynyl)azulene (**10**) and 1,2,3-tris(trimethylsilylethynyl)azulene (**11**), respectively, as green crystals in 90–95% yields. Deprotection of the trimethylsilyl groups of **10** and **11** with potassium hydroxide in methanol and subsequent chromatography on alumina (BII-III) using *n*-hexane as an eluent afforded the 1,2-di- and 1,2,3-triethynylazulenes **1c** and **1e** as greenish blue crystals in 95% and 90% yields, respectively (Scheme 2).

Because of the difficulty of introducing iodosubstituents on the seven-membered ring of azulenes[12] ethynylation of the 5- and 7-position of azulene was achieved by using the Corey–Fuchs[6] method for the conversion of aldehydes into acetylenes. Reaction of the corresponding 5,7-diformylazulene (**12**)[13] with triphenylphosphine and tetrabromomethane in dichloromethane furnished, after chromatography on alumina (BII-III) using *n*-hexane as an eluent, greenish blue crystals of the tetrabromodiolefin **13** in 70% yield. The latter could be converted into the 5,7-diethynylazulene **1h** (86%) upon treatment with 6 equiv. of LDA followed by hydrolysis (Scheme 3).[14]

The ethynylazulenes so far prepared are slightly stable and can be easily manipulated under ambient conditions, especially as long as the alkyne groups are protected by trimethylsilyl groups. With the



Scheme 2. (i) 1 equiv. NIS, CH_2Cl_2, rt; (ii) 2 equiv. NIS, CH_2Cl_2, rt; (iii) 0.04 mol% $PdCl_2(PPh_3)_2$, 0.08 mol% CuI, NEt_3, 1 or 2 equiv. TMSA, rt; (iv) 1.1 equiv. 1 M KOH in H_2O, MeOH, rt



Scheme 3. (i) PPh_3, CBr_4, CH_2Cl_2, rt; (ii) 6 equiv. LDA, THF, −90°C→rt

exception of 5,7-diethynylazulene (**1h**) the deprotected ethynylazulenes **1a**–**e** are only slightly stable at rt and form black solids with metallic luster after a few hours which could not be characterized due to their insolubility. The 6-*tert*-butyl derivatives **1f** and **1g** are noticeably more stable than their unsubstituted derivatives **1a** and **1d** presumably due to the stabilizing effect of the *tert*-butyl groups.

Contrary to alkyl groups, the ethynyl substituents effect in all positions of the bicyclic system a bathochromic shift of the light absorption of azulene due to both inductive and mesomeric effects, respectively.[15]

*Physical data of compounds **1a**, **d**, and **e**.*[16,17] **1a**: blue crystals, m.p. 36–37°C (dec.); HRMS: *m/z*=152.0631; ^{1}H NMR ($CDCl_3$): δ_H=3.51 (s, 1H, -C$\equiv$C-H), 7.25 (t, ^3J=10.0 Hz, 1H, 5-H), 7.27 (t, ^3J=9.6 Hz, 1H, 7-H), 7.30 (d, ^3J=4.0 Hz, 1H, 3-H), 7.67 (t, ^3J=9.8 Hz, 1H, 6-H), 8.00 (s, 1H, 2-H), 8.32 (d, ^3J=9.8 Hz, 1H, 4-H); 8.61 (d, ^3J=9.5 Hz, 1H, 8-H); ^{13}C NMR ($CDCl_3$): δ_C=80.22, 81.39, 109.14, 117.30, 124.10, 124.69, 136.13, 137.26, 138.56, 139.77, 141.27, 142.09; UV–vis (*n*-hexane): λ_{max}=259 nm, 263, 271 sh, 275 sh, 280, 285, 290, 296, 302, 315, 341, 346, 349, 358, 362 sh, 368, 371, 377, 388, 500 sh, 525 sh, 540 sh, 559, 579, 602, 631, 660, 699, 734; **1d**: blue crystals, m.p. 69–71°C (dec.); HRMS: *m/z*=176.0649; ^{1}H NMR ($CDCl_3$): δ_H=3.45 (s, 2H, -C$\equiv$C-H), 7.26 (t, ^3J=10.0 Hz, 2H, 5/7-H), 7.62 (t, ^3J=9.9 Hz, 1H, 6-H), 8.05 (s, 1H, 2-H), 8.49 (d, ^3J=10.0 Hz, 2H, 4/8-H); ^{13}C NMR ($CDCl_3$): δ_C=79.09, 81.06, 108.86, 126.00, 137.5, 139.92, 142.20, 142.24; UV–vis (*n*-hexane): λ_{max}=243 nm sh, 270, 283, 288, 294, 300, 306, 313, 320, 340, 345, 359, 363, 369, 373, 378, 383, 389, 400, 513 sh, 535 sh, 548 sh, 575, 597, 615 sh, 620, 628 sh, 655, 679 sh, 685, 705 sh, 729, 766; **1e**: greenish blue crystals, m.p. 77–78°C; MS (FD): *m/z* (%)=200 (100) [M^+]; ^{1}H NMR ($CDCl_3$): δ_H=3.63 (s, 2H, 1/3-C$\equiv$C-H), 3.90 (s, 1H, 2-C≡C-H), 7.35 (dd, $^3J_1$=9.5 Hz, $^3J_2$=9.5 Hz, 2H, 5/7-H), 7.68 (tt, $^3J_1$=9.9 Hz, 1H, $^5J_2$=1 Hz, 1H, 6-H), 8.50 (d, ^3J=9.3 H, 2H, 4/8-H); ^{13}C NMR ($CDCl_3$): δ_C=77.65, 78.82, 84.17, 89.18, 112.13, 127.12, 134.21, 137,63, 140.61, 141.72; UV–vis (*n*-hexane): λ_{max}=231 nm, 253, 271, 276, 284, 287, 318 sh, 323, 339, 359, 371, 377, 388, 393, 578, 580, 615, 672, 692, 708 sh, 748, 774.

Acknowledgements

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8. 1- and 2-ethynylazulenes (72%) as well as 1,2- and 1,3-diethynylazulenes (23–26%) were also recently prepared from the corresponding aldehydes with lithium trimethylsilyldiazomethane; Fujimori, K. *Abstract 1P31*, *13th Symposium on Fundamental Organic Chemistry*; Nagoya University, Japan Nov. 1–3, 1996, and personal communication.
9. The mono- and diiodoazulenes **2a**, **b** and **3a**, **b** were obtained by reacting the corresponding azulenes with 1 and 2.2 equiv. NIS, respectively, in dichloromethane. The solvent was then removed in vacuo below 10°C followed by chromatography on alumina (BII-III) using *n*-hexane as an eluent. The greenish blue residue was immediately resolved in triethylamine for further cross-coupling reactions. For the synthesis of 1-iodo-and 1-bromoazulene as well as 1,3-dibromoazulene see also: Hafner, K.; Patzelt, H.; Kaiser, H. *Liebigs Ann. Chem*. **1962**, *656*, 24–33. For the synthesis of 2-iodoazulene (**4**) see: Nozoe, T.; Seto, S.; Matsumura, S. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1990–1998.
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11. The trimethylsilylethynylazulenes **5a**, **6a** could also be obtained in 25–35% yields from the Pd-catalyzed cross-coupling reaction of the corresponding bromoazulenes[9] with TMSA in refluxing triethylamine.
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14. Attempts to synthesize **1a**, **b**, **d**, **f** and **g** by the Corey–Fuchs method, starting from the corresponding formylazulenes were unsuccessful presumably due to the deactivation of the carbonyl function at the five-membered ring.
15. Depending on the number and position of the ethynyl groups in the azulene-system the bathochromic shift ranged from 3–48 nm.
16. The described new compounds gave correct elemental analyses.
17. NMR spectra were recorded with a Bruker NMR spectrometer WM 300 in $CDCl_3$ with tetramethylsilane as internal standard. UV–vis spectra were recorded with a Beckman UV-5240 spectrometer. Mass spectra (MS) were obtained with a Varian 311A instrument.