60. An Efficient Straightforward Synthesis of Benz[*a*]azulene

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(15.III.95)

Benz[*a*]azulene (**1**) is synthesized in five steps (*cf. Scheme 2*) starting from commercially available 2-iodobenzyl alcohol (**4**) and tropylium tetrafluoroborate in an overall yield of 44%. The key step (*cf.* also *Scheme 1*) is the intramolecular *Heck* reaction of the 8-phenylsulfonyl-substituted heptafulvene **7**, which leads in nearly quantitative yield directly to 10-(phenylsulfonyl)benz[*a*]azulene (**8**). The desulfonylation of **8** can be accomplished by *Julia*'s method with $Na_2S_2O_4/NaHCO_3$ in DMF/H_2O at 85–90°, thus leading to pure **1** in 78% yield. The phenylation of **8** with PhLi or PhCuI at −78° in THF occurs regioselectively at C(9). Dehydrogenation of the formed dihydroazulenes with *o*-chloroanil in toluene at room temperature gives 9-phenyl-10-(phenylsulfonyl)-benz[*a*]azulene (**9**) in 70% yield (*cf. Scheme 3*), which, again, can be desulfonylated with $Na_2S_2O_4/NaHCO_3$ in DMF/H_2O in good yields. The addition of PhLi to **1** in THF occurs at temperatures $\geq -25°$. Ionic dehydrogenation (1. $Ph_3C^+BF_4^-$/MeCN; 2. Et_3N) of the dihydro forms leads to **3**, as the main product, and its positional isomers.

Introduction. – Since the first synthesis of benz[*a*]azulene (**1**) by *Nunn et al.* in 1947 [1] through dehydratization and dehydrogenation of 4b,5,6,7,8,9,9a,10-octahydrobenz[*a*]-azulen-6-ol, several further syntheses of **1** and its derivatives have been developed, based on intermolecular carbene-addition reactions to fluorene [2] [3] or benzene [4], thermal carbene rearrangements [5], or intramolecular carbene-addition reactions in biphenyl systems [6][2]). Further synthetic approaches to benz[*a*]azulenes have been based on cationic cyclizations of appropriately substituted cycloheptatrienes [8] [9], on [2 + 4]-cycloaddition reactions of cyclopropene with indenocyclanes [10], as well as on [2 + 8]-cycloaddition reactions of heptafulvenes with 1,4-benzoquinones [11] and with arines [12] or of 2*H*-cyclohepta[*b*]furan-2-ones with enamines [13] [14]. Other syntheses of benz[*a*]azulenes start already from azulenes and construct the benzo ring at the azulene skeleton [15] [16]. Recently, *Yasunami et al.* [17] mentioned in a footnote that they have developed a new synthesis of **1** based on the chemistry of 2*H*-cyclohepta[*b*]furan-2-ones.

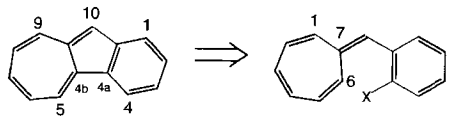
Most of the above mentioned syntheses of benz[*a*]azulene (**1**) or its derivatives are lengthy and lead, in most of the cases, to hydro forms of the desired benz[*a*]azulenes, which, in further steps, have to be decarboxylated, dehydrated, and/or dehydrogenated. As a consequence, the overall yields are often low, and the applied synthetic sequences do not allow very much variations. According to our interest in benz[*a*]azulenes as precursors of benzo[*a*]heptalenes [7] [18–20], which may be useful for the synthesis of colchinoid

[1]) Part of the planned Ph. T. thesis of *D. S.*, University of Zurich.

[2]) *McKervey* and coworkers [6] realized in this way the synthesis of 6-methylbenz[*a*]azulene. In repeating this synthesis, we were not able to accomplish the last step of the described reaction sequence, *i.e.*, the dehydration, accompanied by rearrangement, of 9a,10-dihydro-10-hydroxy-9a-methylbenz[*a*]azulene in aqueous CF_3COOH [7].

compounds with biological activities (*cf.* [21–23]), we were interested in a new efficient and straightforward synthesis of **1**, which would also allow an easy access to its derivatives, carrying substituents at the benzo ring and/or the seven-membered ring. One of the main aims in this context was to end up directly with **1** and not with one of its hydro forms. For this purpose, we studied the intramolecular *Heck* reaction (*cf.* [24]) of appropriately substituted heptafulvenes **2** (*Scheme 1*), in order to form the strategically important C(4a)–C(4b) bond in the crucial reaction step[3]).

Scheme 1



1 **2**[a])

[a]) X = Suitable leaving group for an intramolecular *Heck* reaction.

We report here on our first progresses on a new synthesis of **1** and its 9-phenyl derivative **3**.

Results and Discussions. – The key step of the new synthesis of **1** is the intramolecular *Heck* reaction of the 8-(phenylsulfonyl)-substituted 8-(2-iodophenyl)heptafulvene (**7**), which leads to the formation of 10-(phenylsulfonyl)benz[*a*]azulene (**8**; see step *e* in *Scheme 2*). A yield of up to 92% of **8** can be obtained, when the cyclization is performed under the very mild conditions that have been worked out by *Jeffery* [27] on *Heck* reactions (see also [24])[4]).

The procedure elaborated by *Julia et al.* [28] for the stereospecific reductive desulfonylation of phenyl vinyl sulfones can excellently also be applied for the desulfonylation of **8** (see step *f* in *Scheme 2*) to give **1** in high purity and over 75% yield.

The required heptafulvene **7** was synthesized in three steps starting from commercially available 2-iodobenzyl alcohol (**4**) and tropylium tetrafluoroborate. Reaction of the bromide of **4** with sodium phenylsulfinate in DMF gave the sulfone **5**, the α-carbanion of which could be alkylated nearly quantitatively with tropylium tetrafluoroborate, in line with comparable alkylation reactions that have been investigated by *Makosza* and *Ostrowski* [29]. The resulting cycloheptatrienyl-substituted sulfone **6** was transformed into **7** in a one-pot reaction (see step *d* in *Scheme 2*), consisting of deprotonation at −78° with *t*-BuOK in THF, chlorination of the formed α-carbanion with hexachloroethane at −78°, and elimination of HCl with *t*-BuOK/THF at room temperature. The yield of **7**, over all three steps, amounted to 57%. In total, the yield of **1**, starting from **4**, amounts to 44%, following the steps described in *Scheme 2*.

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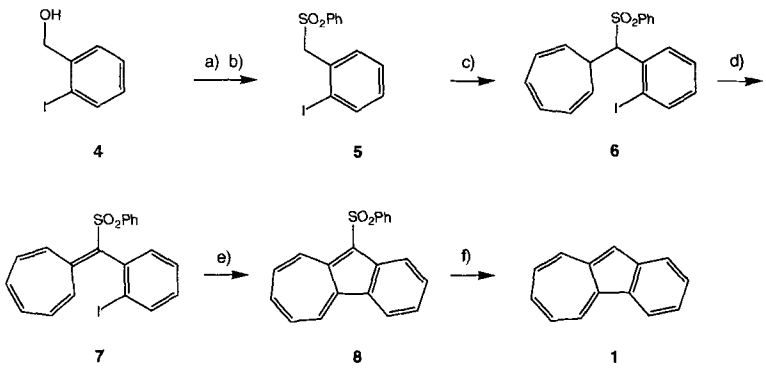
[3]) Over the past ten years, the intramolecular *Heck* reaction had turned out as one of the most versatile synthetic tools for ring formations (*cf.* [24]). However, there are only a few examples known where aromatic systems are formed by Pd-catalyzed ring closure of appropriately designed olefinic precursors (*cf.* Chapt. 7.6. in [24]). 1,2,3,4-Tetrahydrocarbazols [25] have been formed catalytically in intramolecular *Heck* reactions at temperatures > 120° (*cf.* also [26]).

[4]) The *Heck* cyclization reaction of **7** is not suppressed in the presence of 1.5 equiv. of PhI. This indicates that Pd^0-complex formation takes place at the heptafulvene structure of **7** prior to the oxidative addition of Pd^0 to the Ar–I bond (*cf.* [24]).

Scheme 2

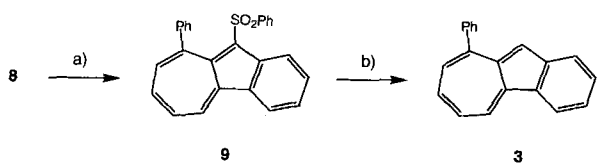


a) HBr/AcOH. b) $PhSO_2Na$/DMF, 80°; 86%. c) 1. *t*-BuOK/THF, −78°; 2. $C_7H_7^+BF_4^-$/DMF, room temp.; 95%. d) 1. *t*-BuOK/THF, −78°; 2. C_2Cl_6/THF, −78°; 3. *t*-BuOK/THF, r.t.; 75%. e) 0.5 mol-% $Pd(OAc)_2$, $Bu_4N^+Cl^-$, $NaHCO_3$/DMF, r.t./30 h; 92%. f) $Na_2S_2O_4$, $NaHCO_3$/DMF + H_2O, 85–90°/17 min; 78%.

Since the *Heck* reaction with iodobenzenes is not very dependent on substituents at the benzene ring (*cf.* [24] [26]), we suppose that the new synthesis will also be applicable to benz[*a*]azulenes carrying substituents at C(1) to C(4). However, it might be difficult to work with substituted tropylium salts, since mixtures of positional isomers of cycloheptatrienyl-substituted sulfones of type **6** have to be expected in the alkylation step. Nevertheless, the alkylation of the seven-membered ring of azulenes at C(4), C(6), and/or C(8) by RLi (R = alkyl or aryl), followed by dehydrogenation of the primarily formed dihydroazulenes, is a well established method (*cf.* [30–32]) for the synthesis of azulenes, bearing alkyl or aryl substituents at C(4), C(6), and/or C(8).

To demonstrate that this procedure can also be applied to the synthesis of benz[*a*]azulenes, substituted at the seven-membered ring, we investigated the arylation reaction of **8** with PhLi in THF (*Scheme 3*). The solution of **8** in THF at −78° was titrated with a 2M solution of PhLi in cyclohexane/Et_2O 7:3, until the color had changed from dark-violet to yellow. After hydrolysis, the crude dihydroazulene mixture was directly dehydrogenated with *o*-chloroanil in toluene at room temperature. The resulting 9-phenylated azulene **9** was isolated in a yield of 70%[5][6]. The desulfonylation of **9** could again be accomplished with $Na_2S_2O_4$/$NaHCO_3$ in DMF/H_2O in a yield of 72%. That the Ph group

Scheme 3



a) 1. PhLi/THF, −78°; 2. 3,4,5,6-tetrachloro-1,2-benzoquinone (*o*-chloroanil)/toluene, r.t.; 70%. b) $Na_2S_2O_4$, $NaHCO_3$/DMF + H_2O, 85–90°/20 min; 72%.

[5]) The same results were obtained with PhCuI as phenylation agent for **8**.

[6]) Other dehydrogenation procedures have not been checked so far.

has entered the seven-membered ring of **8** exclusively at C(9) is evident from a comparison of the ^{1}H-NMR spectra ($CDCl_3$) of **8** and **9**. Azulene **8** shows the resonance signal of H–C(9) as a *d* (^3J(H–C(8),H–C(9)) = 10.9 Hz)[7]), most strongly deshielded, at 9.51 ppm, followed by the resonance signal of H–C(4) (*d*, ^3J(H–C(3),H–C(4)) = 8.7 Hz) at 8.74 ppm. In contrast to these findings, in the ^{1}H-NMR spectrum of **9**, no resonance signal is observed above 8.8 ppm, and H–C(4) appears as a *d* (^3J(H–C(3),H–C(4)) = 8.5 Hz) at 8.78 ppm.

In principle, benz[*a*]azulene (**1**) itself can also be reacted with PhLi in THF. However, the temperature has to be raised to –25° for completion of the addition reaction. In this case, the obtained mixture of dihydroazulenes was dehydrogenated by hydride abstraction with $Ph_3C^+BF_4^-$/MeCN, followed by deprotonation with Et_3N, leading to **3** in a mixture with *ca.* 20% of other phenylated isomers of **3**. The work will be continued.

We thank Dr. *Ch. Weymuth* for helpful discussions on synthetic problems, Prof. *M. Hesse* and his coworkers for mass spectra, Prof. *W. von Philipsborn* and his coworkers for NMR support, and *H. Frohofer* and *J. Kessler* for elemental analyses. The financial support of this work by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* is gratefully acknowledged.

Experimental Part

General. All reactions were performed under N_2. All solvents were distilled before use according to [35]; anh. THF was freshly distilled from benzophenone sodium, *t*-BuOK (*Fluka, pract.*) was used without further purification. Column chromatography (CC): silica gel (*Merck*; 40–63 μm). TLC: silica gel on glass plates (*60 F_{254}, Merck*). M.p.: *Büchi* apparatus (model *FP5*); values are not corrected. UV Spectra: *Otsuka* spectrophotometer (model *MCPD 1100*). IR Spectra: *Perkin-Elmer* spectrophotometer (model *FT-IR 1600*). ^{1}H- and ^{13}C-NMR Spectra: *Bruker* instruments (models *AC 300* and *AC 600*); m_c centered multiplet.

1. *2-Iodobenzyl Phenyl Sulfone* (**5**). *2-Iodobenzyl alcohol* (**4**; *Fluka, purum*; 15.03 g, 64.20 mmol) was suspended in a vigorously stirred soln. of glacial AcOH (70 ml) and HBr (8M in H_2O, 70 ml). The suspension was heated up to 80°. Alcohol **3** became slowly dissolved. After 2 min further stirring, the clear soln. became turbid due to the separation of 2-iodobenzyl bromide. Stirring was continued for further 10 min at 80°. The mixture was poured on ice-water and stirred again for 10 min. The precipitate was filtered, washed until the washings became neutral, and then dried *in vacuo*. The colorless powder of 2-iodobenzyl bromide (18.53 g, 97%) was used without further purification. It (17.26 g, 57.92 mmol) was dissolved in DMF (100 ml) at 80° and $PhSO_2Na$ (*Fluka, purum*; 14.26 g, 86.88 mmol) added in portions. This suspension was stirred at 80° for 10 min, then poured into H_2O (500 ml) and stirred vigorously for 30 min. The precipitate was filtered, washed with H_2O and dried *in vacuo*. Recrystallization from CH_2Cl_2/hexane yielded **5** (17.80 g, 86%) in bright colorless needles.

Data of **5**: M.p. 132.6–133.2°. R_f (hexane/Et_2O 1:1) 0.2 (R_f 0.85 (2-iodobenzyl bromide)). IR (KBr): 3059*w*, 2976*m*, 2927*m*, 1921*w*, 1580*w*, 1561*m*, 1470*m*, 1447*s*, 1433*m*, 1413*m*, 1309*s* (SO_2), 1265*s* (SO_2), 1242*m*, 1195*w*, 1165*m*, 1146*s*, 1094*m*, 1062*s*, 1045*m*, 1025*m*, 1009*s*, 996*m*, 948*w*, 930*m*, 892*w*, 667*w*, 821*m*, 777*m*, 759*s*, 729*s*, 691*s*, 645*m*, 613*s*, 552*s* (Ph-I), 521*s* (Ph-I), 482*m*, 450*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.73 (*dd*, ^3J = 8.0, ^4J = 0.9, 1 H); 7.60–7.66 (*m*, 3 H); 7.43–7.25 (*m*, 3 H); 7.35 (*td*, ^3J = 7.6, ^4J = 1.0, 1 H); 7.00 (*td*, ^3J = 7.7, ^4J = 1.6, 1 H); 4.59 (*s*, 2 H). EI-MS: 358 (5, $M^{+\cdot}$), 231 (17, $[M - HI]^+$), 217 (93, $[M - HSO_2Ph]^+$), 90 (100). CI-MS (NH_3): 376 (100, $[M + NH_4]^+$), 248 (14). Anal. calc. for $C_{13}H_{11}IO_2S$ (358.18): C 43.59, H 3.09; found: C 43.54, H 3.30.

2. *7-[(2-Iodophenyl)(phenylsulfonyl)methyl]-1,3,5-cycloheptatriene* (**6**). To a soln. of **5** (9.14 g, 25.54 mmol) in THF (100 ml) at –78° was added a soln. of *t*-BuOK (3.45 g, 30.65 mmol) in THF (20 ml) and stirred for 5 min while maintaining –78°. The resulting bright-yellow soln. was transferred to a soln. of tropylium tetrafluoroborate (*Fluka, purum*; 6.00 g, 33.71 mmol) in DMF (150 ml) at r.t. using a *Teflon* cannula. The transfer time was *ca.* 1 min. The resulting slightly brown soln. was stirred for 15 min at r.t. and then poured into a stirred sat. aq. $NaHCO_3$ ice mixture (1:1, 500 ml). Stirring was continued for 30 min. The precipitate was filtered, washed with H_2O, and dried

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[7]) The ^{1}H- and ^{13}C-NMR spectra of **1** and of the new benz[*a*]azulenes **3**, **8**, and **9**, will be analyzed later [33] (*cf.* also [34]).

in vacuo. An isothermal crystallization at r.t. from CH_2Cl_2 with Et_2O yielded **6** (10.03 g, 96%) in colorless rhombic crystals.

Data of **6**: M.p. 166.7–167.8°. R_f (hexane/Et_2O 1:1) 0.58. IR (KBr): 3428*w*, 3060*w*, 3014*m*, 2922*w*, 2872*w*, 1948*w*, 1769*w*, 1690*w*, 1584*m*, 1563*w*, 1522*w*, 1466*m*, 1446*s*, 1426*m*, 1396*m*, 1351*w*, 1306*s* (SO_2), 1286*s*, 1252*m*, 1230*m*, 1219*m*, 1184*m*, 1140*s* (SO_2), 1082*s*, 1013*s*, 998*s*, 952*w*, 881*w*, 819*s*, 795*m*, 756*s*, 740*s*, 716*s*, 703*s*, 687*s*, 659*m*, 618*m*, 589*s*, 551*s*, 513*m*, 456*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.68 (*dd*, $J_o = 7.9$, $J_m = 1.2$, H–C(6 or 3) of C_6H_4I); 7.5–7.6 (*m*, 3 H); 7.47 (*dd*, $J_o = 7.9$, $J_m = 1.7$, H–C(3 or 6) of C_6H_4I); 7.35 (m_c, 3 H); 6.96 (*ddd*, $J_o = 7.9$, $J_o = 7.3$, $J_m = 1.7$, H–C(4 or 5) of C_6H_4I); 6.77 (*ddd*, $^3J = 10.4$, $^3J = 5.52$, $^4J < 1$, H–C(4 or 3)); 6.68 (*ddq*-like, $^3J = 10.5$, $^3J = 5.5$, ^4J or $^5J < 1$, H–C(3 or 4)); 6.27 (*ddqi*-like, $^3J = 9.5$, $^3J = 5.5$, H–C(5 or 2)); 6.04 (*ddqi*-like, $^3J = 9.5$, $^3J = 5.5$, H–C(2 or 5)); 5.79 (*dd*, $^3J = 9.4$, $^3J = 6.4$, H–C(6 or 1)); 5.08 (*d*, $^3J = 11.2$, C*H*SO_2); 4.76 (*dd*, $^3J = 9.3$, $^3J = 6.7$, H–C(1 or 6)); 3.04 (*dt*, $^3J = 11.2$, $^3J = 6.5$, H–C(7)). ^{13}C-NMR (75 MHz, $CDCl_3$): 39.97 (*d*); 74.36 (*d*); 105.00 (*s*); 118.73 (*d*); 122.38 (*d*); 124.92 (*d*); 125.55 (*d*); 128.50 (*d*, double intensity); 128.65 (*d*); 129.26 (*d*, double intensity); 130.04 (*d*); 130.21 (*d*); 130.88 (*d*); 131.28 (*d*); 133.59 (*d*); 135.52 (*s*); 138.49 (*s*); 139.75 (*d*). CI-MS (NH_3): 466 (100, $[M + NH_4]^+$). Anal. calc. for $C_{20}H_{17}IO_2S$ (448.32): C 53.57, H 3.82; found: C 53.35, H 3.66.

3. *7-[(2-Iodophenyl)(phenylsulfonyl)methylidene]-1,3,5-cycloheptatriene* (= *8-(2-Iodophenyl)-8-(phenylsulfonyl)heptafulvene*) (**7**). The sulfone **6** (8.27 g, 18.41 mmol) was dissolved in THF (100 ml) and a soln. of *t*-BuOK (2.48 g, 22.10 mmol) in THF (25 ml) was added while keeping the temp. at −78°. The resulting bright-yellow soln. was stirred at −78° for 5 min. Then, a soln. of Cl_3CCCl_3 (*Fluka, purum*; 5.66 g, 23.94 mmol) in THF (30 ml) was rapidly added. The pale-yellow soln. was stirred for 5 min at −78°, and then, glacial AcOH (0.21 ml, 3.68 mmol) was added dropwise at −78°. The mixture was warmed up to *ca.* 30° within 3 min. A soln. of *t*-BuOK (3.09 g, 27.62 mmol) in THF (30 ml) was added within 2 min, and stirring was continued for 15 min. The resulting dark-red soln. was poured into sat. aq. $NaHCO_3$/ice and then extracted with Et_2O. The Et_2O phases were washed with H_2O and then concentrated at 40° to a volume of *ca.* 150 ml. Toluene (100 ml) was added, and the soln. again concentrated at 40° to 150 ml. This procedure was repeated three times with the intention to remove the tetrachloroethylene, formed in the chlorination reaction. Toluene was removed completely and the crude product dissolved in Et_2O, whereupon **7** (4.80 g, 58%) separated in dark-red needles. The mother liquor was subjected to CC (hexane/CH_2Cl_2 1:1) yielding a second crop of crystalline **7** (1.40 g, 17%, in total 75%).

Data of **7**: M.p. 115.2–117.0°. R_f (hexane/Et_2O 1:1) 0.37. UV/VIS (CH_2Cl_2): λ_{max} 352.4 (4.20), λ_{min} 294.0 (3.50). IR (KBr): 3056*w*, 2253*w*, 1636*w*, 1548*m*, 1509*m*, 1458*m*, 1446*m*, 1420*w*, 1301*s* (SO_2), 1231*w*, 1200*w*, 1142*s* (SO_2), 1082*m*, 1047*w*, 1013*w*, 950*w*, 906*s*, 884*w*, 852*m*, 816*w*, 724*s*, 688*m*, 668*m*, 647*m*, 636*m*, 619*m*, 584*s*, 549*s*, 502*w*, 476*m*, 467*w*, 455*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.94 (*ddt*, $^3J(6,5) = 11.2$, $^4J(6,1) = 2.6$, $^4J(6,4) \approx {}^5J(6,3) \approx 1$, H–C(6)); 7.84 (*dd*, $J_o = 8.0$, $J_m = 1.2$, H–C(3) of C_6H_4I); 7.72 (*d* with f.s., $J_o = 8.2$, H–C(2,6) of $PhSO_2$); 7.54 (*tt*, $J_o = 7.4$, $J_m = 1.3$, H–C(4) of $PhSO_2$); 7.41 (*t* with f.s., $J_o = 7.8$, H–C(3,5) of $PhSO_2$); 7.36 (*td*, $J_o = 7.5$, $J_m = 1.2$, H–C(5) of C_6H_4I); 7.19 (*dd*, $J_o = 7.7$, $J_m = 1.8$, H–C(6) of C_6H_4I); 7.01 (*td*, $J_o = 7.5$, $J_m = 1.9$, H–C(4) of C_6H_4I); 6.59 (*ddd*, $^3J(2,1) = 11.5$, $^3J(2,3) = 7.4$, $^4J(2,4) = 1.4$, H–C(2)); 6.47 (*t* with f.s., $^3J = 9.0$, H–C(3 or 4)); 6.35 (*t* with f.s., $^3J = 9.0$, H–C(4 or 3)); 6.22 (*ddd*, $^3J(5,6) = 11.9$, $^3J(5,4) = 7.3$, $^4J(5,3) = 1.3$, H–C(5)); 5.77 (*ddt*, $^3J(1,2) = 11.2$, $^4J(1,6) = 2.6$, $^4J(1,3) \approx {}^5J(1,4) \approx 1$, H–C(1)). ^{13}C-NMR (75 MHz, $CDCl_3$): 103.72 (*s*); 127.86 (*d*, double intensity); 128.38 (*d*, triple intensity); 129.68 (*d*); 130.21 (*d*); 131.51 (*s*); 132.09 (*d*); 132.30 (*d*); 132.44 (*d*); 132.60 (*d*, double intensity); 132.69 (*d*); 133.46 (*d*); 138.70 (*s*); 139.67 (*d*); 141.09 (*s*); 145.99 (*s*). EI-MS: 446 (11, M^+), 321 (5, $[M - HI]^+$), 178 (100, $[M - HI - HSO_2Ph]^+$), 152 (25), 151 (24), 77 (57). Anal. calc. for $C_{20}H_{15}IO_2S$ (446.31): C 53.82, H 3.39; found: C 53.56, H 3.39.

4. *10-(Phenylsulfonyl)benz[a]azulen* (**8**). The heptafulvene **7** (3.19 g, 7.12 mmol), $Pd(OAc)_2$ (*Fluka, purum*; 0.0104 g, 0.0463 mmol), $NaHCO_3$ (1.55 g, 18.41 mmol), and Bu_4NCl (2.10 g, 7.12 mmol) were dissolved in DMF (150 ml) and stirred 30 h at r.t. The dark-violet soln. was poured into cold water (500 ml) and stirred during 30 min at r.t. The precipitate was filtered and dissolved in a small quantity of CH_2Cl_2. The soln. was filtrated over *Alox* (Act. III) and subjected to an isothermal crystallization using CH_2Cl_2/Et_2O: **8** (2.09 g, 92%) crystallized in green, fluffy needles.

Data of **8**: M.p. 194.5–195.5°. R_f (hexane/Et_2O 1:1) 0.25. UV/VIS (CH_2Cl_2): λ_{max} 542.8 (2.64), 418.4 (3.81), 395.2 (3.79), 381.6 (3.72), 361.6 (3.61), 325.6 (4.52), 285.6 (4.28); λ_{min} 454.0 (2.37), 406.8 (3.71), 337.6 (4.49), 300.4 (4.25). IR (KBr): 3067*w*, 1597*m*, 1518*m*, 1486*m*, 1476*m*, 1446*s*, 1393*s*, 1371*s*, 1319*m*, 1300*s* (SO_2), 1288*s*, 1266*m*, 1245*w*, 1218*m*, 1180*w*, 1140*s* (SO_2), 1083*s*, 1024*w*, 998*w*, 978*w*, 956*w*, 943*w*, 905*m*, 885*m*, 861*w*, 839*w*, 756*s*, 721*s*, 696*s*, 657*m*, 602*s*, 578*s*, 542*s*, 506*w*, 452*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 9.51 (*d*, $^3J = 10.9$, H–C(9)); 8.74 (*d*, $^3J = 8.7$, H–C(4)); 8.58 (*d*, $^3J = 7.9$, H–C(1)); 8.36 (*d*, $^3J = 8.3$, H–C(5)); 8.05 (*d*, $J_o = 7.64$, H–C(2,6) of $PhSO_2$); 7.77 (*t*, $^3J = 7.6$, H–C(2)); 7.67 (*t*, $^3J = 9.8$, H–C(7)); 7.56–7.49 (3*t* overlapping, H–C(3), H–C(6), H–C(8)); 7.43 (*t*, $J_o = 7.0$, H–C(4) of $PhSO_2$); 7.39 (*t*, $J_o = 7.7$, H–C(3,5) of $PhSO_2$). ^{1}H-NOE (600 MHz): 9.51 (H–C(9)) → 7.55

(*s*, H–C(8)), 8.05 (*w*, H–C(2,6) of $PhSO_2$); 8.74 (H–C(4)) → 8.36 (*s*, H–C(5)), 7.53 (*s*, H–C(3)); 8.58 (H–C(1)) → 7.77 (*s*, H–C(2)), 8.05 (*w*, H–C(2,6) of $PhSO_2$); 8.36 (H–C(5)) → 8.74 (*s*, H–C(4)), 7.56–7.49 (*s*, H–C(6)); 8.05 (H–C(2,6) of $PhSO_2$) → 9.51 (*w*, H–C(9)), 8.58 (*w*, H–C(1)), 7.39 (*s*, H–C(3,5) of $PhSO_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): 143.93 (*s*); 141.37 (*s*); 141.20 (*s*); 138.99 (*d*); 137.79 (*d*); 134.54 (*d*); 132.67 (*d*); 132.41 (*d*); 130.23 (*d*, double intensity); 129.92 (*s*); 129.28 (*s*); 128.86 (*d*, double intensity); 125.81 (*d*, double intensity); 123.22 (*d*); 120.87 (*d*); 120.48 (*d*); 117.61 (*s*). EI-MS: 318 (8, M^+), 193 (71), 176 (65, $[M - HSO_2Ph]^+$), 165 (49), 77 (100). Anal. calc. for $C_{20}H_{14}O_2S$ (318.40): C 75.45, H 4.43; found: C 75.22, H 4.58.

5. *Benz[a]azulene* (**1**). Compound **8** (0.502 g, 1.57 mmol), $Na_2S_2O_4$ (0.546 g, 3.14 mmol), and $NaHCO_3$ (0.527 g, 6.28 mmol) were dissolved in DMF (30 ml), and H_2O (20 ml) was added. The turbid suspension of brown-green color was stirred and heated at 85–90°. The color of the mixture changed to dark-green, to dark-violet and then to dark-blue. As soon as the soln. was clear, and no further **8** could be detected (15 min, TLC, toluene), the mixture was poured into ice/water (500 ml). The resulting green soln. was saturated with NaCl, stirred for 15 min, and the precipitate filtered off. The residue was dissolved in a few ml of CH_2Cl_2, then hexane (100 ml) was added and the soln. concentrated to 100 ml. This soln. was filtered over *Alox* (Akt. III) and eluted with hexane. The elute was concentrated to *ca.* 100 ml and left at r.t. for 3 h, and then overnight at −4°: **1** (0.28 g, 78%) separated in black-green plates.

Data of **1**: M.p. 191–192° ([32] [4]: 189–190°). R_f (hexane) 0.28. IR (KBr): 3043*m*, 2955*m*, 2924*m*, 1601*s*, 1585*m*, 1521*m*, 1447*m*, 1432*m*, 1396*m*, 1376*m*, 1323*m*, 1263*m*, 1238*s*, 1198*m*, 1157*s*, 1012*s*, 932*m*, 852*m*, 809*s*, 762*s*, 733*s*, 682*s*, 577*w*. ^{1}H-NMR (600 MHz, $CDCl_3$)[8]: 8.38 (*ddd*, $^3J(3,4) = 7.9$, $^4J(2,4) = 1.8$, $^5J(1,4) = 0.9$, H–C(4)); 8.30 (br. *dd*, $^3J(5,6) = 8.3$, $^4J(5,7) = 1.0$, H–C(5)); 7.95 (*ddd*, $^3J(8,9) = 10.9$, $^4J(7,9) = 1.7$, $^5J(6,9) = 1.0$, H–C(9)); 7.88 (*ddd*, $^3J(1,2) = 7.9$, $^4J(1,3) = 1.9$, $^5J(1,4) = 1.0$, H–C(1)); 7.67 (*ddd*, $^3J(2,3) = 9.3$, $^3J(1,2) = 7.9$, $^4J(2,4) = 1.9$, $^5J = 1.0$, H–C(2)); 7.48 (*ddd*, $^3J(2,3) = 9.3$, $^3J(3,4) = 7.9$, $^4J(1,3) = 1.9$, $^5J = 1.0$, H–C(3)); 7.33 (br. *s*, H–C(10)); 7.19 (*dddd*, $^3J(6,7) = 11.1$, $^3J(7,8) = 8.5$, $^4J(5,7) = 1.7$, $^4J(7,9) = 1.0$, H–C(7)); 7.04 (*ddt*, $^3J(6,7) = 11.1$, $^3J(5,6) = 8.3$, $^4J(6,8) \approx {}^4J(6,9) < 1.0$, H–C(6)); 6.84 (*ddt*, $^3J(8,9) = 10.9$, $^3J(7,8) = 8.5$, $^4J(6,8) \approx {}^4J(8,10) \approx 0.8$, H–C(8)). ^{13}C-NMR (75 MHz, $CDCl_3$): 142.40 (*s*, C(10a)); 140.58 (*s*, C(4b)); 139.20 (*s*, C(9a)); 135.94 (*d*, C(9)); 134.64 (*d*, C(7)); 131.41 (*s*, C(4a)); 128.48 (*d*, C(2)); 127.86 (*d*, C(5)); 125.35 (*d*, C(6)); 123.66 (*d*, C(8)); 121.78 (*d*, C(3)); 120.78 (*d*, C(4)); 120.25 (*d*, C(1)); 116.06 (*d*, C(10)). EI-MS: 178 (100, M^+), 176 (15), 152 (11). Anal. calc. for $C_{14}H_{10}$ (178.24): C 94.34, H 5.66; found: C 94.54, H 5.67.

6. *9-Phenyl-10-(phenylsulfonyl)benz[a]azulene* (**9**). To a soln. of **8** (0.103 g, 0.323 mmol) in THF (10 ml) at −78° was added PhLi (2M in cyclohexane/Et_2O 7:3), until the color changed from dark-violet to pale-yellow. To the resulting mixture was added MeOH (*ca.* 2 drops), and the mixture was poured into sat. aq. NH_4 soln. The soln. was extracted with Et_2O. The Et_2O extracts were dried (Na_2SO_4) and the solvent removed. The residue was dissolved in toluene (20 ml), *o*-chloroanil (0.080 g, 0.419 mmol) was added and the mixture stirred for 16 h at r.t. The brown-yellow suspension was filtered and the precipitate washed with H_2O and then, with Et_2O. Recrystallization from CH_2Cl_2 yielded **9** (0.089 g, 70%) in fine black needles.

Data of **9**: M.p. 214.0–215.5°. R_f (CH_2Cl_2) 0.39. UV/VIS (CH_2Cl_2): λ_{max} 466.0 (2.74, sh), 424.8 (3.68, sh), 399.6 (3.76, sh), 364.0 (4.03); λ_{min} 278.0 (4.16). IR (KBr): 3065*m*, 3051*m*, 1599*s*, 1567*m*, 1560*m*, 1500*m*, 1472*s*, 1444*s*, 1406*s*, 1379*s*, 1360*s*, 1314*s*, 1297*s*, 1277*s*, 1229*s*, 1192*m*, 1162*w*, 1138*s*, 1116*m*, 1085*s*, 1024*m*, 1001*m*, 956*s*, 930*s*, 908*m*, 893*s*, 844*m*, 781*m*, 762*s*, 754*s*, 738*s*, 729*s*, 718*s*, 700*s*, 685*s*, 653*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.78 (br. *d*, $^3J(3,4) = 8.5$, H–C(4)); 8.41 (*d*, $^3J(1,2) = 8.2$, H–C(1)); 8.38 (*d*, $^3J(5,6) = 8.2$, H–C(5)); 7.75 (*td*, $^3J(1,2) = 7.6$, $^4J(2,4) = 1.2$, H–C(2)); 7.6–7.4 (*m*, 7 H); 7.25 (*tt*-like, $J_o = 7.5$, H–C(3,5) of $PhSO_2$); 7.14 (br. *d*, $J_o = 7.0$, H–C(2,6) of Ph); 7.04 (*tt*, $J_o = 7.4$, $J_m = 1.3$, H–C(4) of Ph); 6.89 (*t*, $J_o = 7.8$, H–C(3,5) of Ph). ^{13}C-NMR (75 MHz, $CDCl_3$): 119.58 (*d*); 120.59 (*d*); 122.95 (*d*); 124.15 (*d*, double intensity); 126.90 (*d*, fourfold intensity); 127.48 (*d*, double intensity); 127.66 (*d*, double intensity); 127.96 (*d*); 129.25 (*s*); 129.56 (*d*); 131.00 (*d*); 131.64 (*d*); 134.73 (*d*); 135.05 (*d*); 140.85 (*s*); 140.90 (*s*); 143.12 (*s*); 144.22 (*s*); 145.30 (*s*); 149.06 (*s*). EI-MS: 394 (9, M^+), 253 (100, $[M - HSO_2Ph]^+$). Anal. calc. for $C_{26}H_{18}O_2S$ (394.49): C 79.16, H 4.59; found: C 78.94, H 4.80.

7. *9-Phenylbenz[a]azulene* (**3**). 7.1. Via **9**. Compound **9** (0.127 g, 0.322 mmol), $Na_2S_2O_4$ (0.112 g, 0.644 mmol), and $NaHCO_3$ (0.108 g, 1.287 mmol) in DMF (10 ml) and H_2O (3 ml) were stirred at 85–90° in analogy to *5*. Workup yielded **3** (0.057 g, 70%) in dark-blue needles.

7.2. *By Direct Phenylation of* **1**. To a soln. of **1** (0.102 g, 0.322 mmol) in THF (10 ml) at −25° was added PhLi (0.24 ml (0.486 mmol) of a 2M soln. in cyclohexane/Et_2O 7:3) and stirred for 15 min. To the resulting mixture was added MeOH (*ca.* 2 drops), and the mixture was poured into sat. aq. NH_4Cl soln. The soln. was extracted with

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[8]) The assignments are based on ^{1}H,^{1}H-TOCSY and $J(^1H,^{13}C)$ long-range measurements and differ from those reported by *Bertelli* and *Crews* [34] (*cf.* [33]).

Et_2O. The Et_2O extracts were dried (Na_2SO_4), and the solvent was removed. The residue was dissolved in MeCN (20 ml), $(Ph)_3C^+BF_4^-$ (0.106 g, 0.323 mmol) was added, and the mixture stirred for 20 min at 80°. The mixture was cooled to r.t., Et_3N (0.5 ml) added, and the soln. was stirred for 5 min. The solvent was removed. The residue was subjected to CC (*Alox* (Act. III), hexane) yielding **3** (0.033 g, 40%) in dark-blue needles.

Data of **3**: M.p. 91.5–92.5°. R_f (hexane) 0.16. UV/VIS (CH_2Cl_2): λ_{max} 406.0 (3.41), 385.2 (3.64), 366.8 (3.59), 310.0 (4.65), 294.0 (4.54); λ_{min} 400.0 (3.23), 376.4 (3.47), 356.0 (3.45), 258.0 (4.21). IR (KBr): 3043*m*, 1944*w*, 1618*w*, 1597*s*, 1579*m*, 1570*m*, 1514*w*, 1489*m*, 1474*m*, 1443*s*, 1407*s*, 1396*s*, 1360*m*, 1308*m*, 1236*m*, 1198*m*, 1125*w*, 1105*w*, 1074*w*, 1062*w*, 1025*m*, 933*w*, 920*m*, 825*m*, 818*s*, 765*s*, 751*s*, 732*s*, 710*s*, 700*s*, 567*m*, 527*m*, 490*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.42 (*dt*, $^3J(5,6) = 8.4$, $^4J(5,7) \approx {}^5J(5,10) \approx 1.0$, H–C(5)); 8.40 (*dq*-like, $^3J(3,4) = 7.8$, $^4J(2,4) \approx 2 \cdot {}^5J(1,4)$, H–C(4)); 7.75 (*dt*-like, $^3J(1,2) = 7.8$, $^4J(1,3) \approx 2 \cdot {}^5J(1,4)$, H–C(1)); 7.64 (*td*, $^3J(1,2) \approx {}^3J(2,3) = 7.1$, $^4J(2,4) = 1.0$, H–C(2)); 7.60–7.48 (*m*, 6 H); 7.27 (*ddd*, $^3J(6,7) = 11.0$, $^3J(7,8) = 8.9$, $^4J(5,7) = 1.0$, H–C(7)); 7.06 (br. *s*, H–C(10)); 7.05 (*ddd*, $^3J(6,7) = 11.0$, $^3J(5,6) = 8.4$, $^4J \approx 1.0$, H–C(6)); 6.85 (br. *d*, $^3J(7,8) = 8.9$, H–C(8)). ^{13}C-NMR (75 MHz, $CDCl_3$): 156.81 (*s*); 151.54 (*s*); 149.58 (*s*); 148.80 (*s*); 146.23 (*s*); 141.75 (*d*); 139.61 (*s*); 136.31 (*d*, double intensity); 136.14 (*d*, double intensity); 136.03 (*d*); 135.87 (*d*); 135.52 (*d*); 133.52 (*d*); 132.02 (*d*); 129.67 (*d*); 128.34 (*d*); 128.15 (*d*); 125.11 (*d*). EI-MS: 254 (100, $M^{+\cdot}$), 253 (58), 252 (58), 250 (18). Anal. calc. for $C_{20}H_{14}$ (254.33): C 94.45, H 5.55; found: C 94.17, H 5.78.

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