142. Radical Arylation Reactions of 4,6,8-Trimethylazulene

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The synthesis of 1- and 2-aryl-substituted (aryl = Ph, 4-NO_2–C_6H_4, and 4-MeO–C_6H_4) 4,6,8-trimethylazulenes (**4** and **3**, respectively) in moderate yields by direct arylation of 4,6,8-trimethylazulene (**8**) with the corresponding arylhydrazines **13** in the presence of Cu^{II} ions in pyridine (see *Scheme 4*) as well as with 4-MeO–$C_6H_4Pb(OAc)_3$ (**16**) in CF_3COOH (see *Scheme 5*) is described. With **13**, also small amounts of 1,2- and 1,3-diarylated azulenes (see **14** and **15**, respectively, in *Scheme 4*) are formed. The 4-methoxyphenylation of **8** with **16** yielded also the 1,1′-biazulene **17** in minor amounts (see *Scheme 5*). 4,6,8-Trimethyl-2-phenylazulene (**3a**) was also obtained as the sole product in moderate yields by the reaction of sodium phenylcyclopentadienide (**1a**) with 2,4,6-trimethylpyrylium tetrafluoroborate (**2**) in THF (*Scheme 1*). The attempted phenylation of **8** as well as of azulene (**9**) itself with *N*-nitroso-*N*-phenylacetamide (**10**) led only to the formation of the corresponding 1-(phenylazo)-substituted azulenes **12** and **11**, respectively (*Scheme 3*).

1. Introduction. – In most of the aryl-substituted azulenes that have been prepared in the nearly 60-year-old history of azulene synthesis (*cf.* [1] [2]), the aryl groups were already present in the reactants that were combined to azulenes[2]). A direct arylation method of azulenes has been developed by *Hafner et al.* [17–19] who showed that aryllithium derivatives can be added directly to the seven-membered ring of azulenes. The dihydroazulenes, formed as intermediates, can easily be dehydrogenated to the corresponding azulenes. However, this LUMO(azulene)-controlled reaction allows the nucleophilic addition only at C(4), C(6), and C(8). Also the reaction of diethyl azulene-1,3-dicarboxylate or of its 2-chloro derivative with aryl-*Grignard* reagents leads mainly to the formation of the corresponding 4- and 6-arylated azulene-1,3-dicarboxylate [20] [21]. However, diethyl 2-methoxyazulene-1,3-dicarboxylate is first phenylated at C(2) and than mainly at C(4) with PhMgBr [21].

In the course of our investigations of possible thermo- and photochromisms of heptalenes [22], we were interested in the synthesis of 4- and 5-aryl-substituted heptalene-1,2-dicarboxylates with at least three substituents in the *peri*-positions to slow down the thermal C=C bond shift in these heptalenes (see [23–26]). Starting materials for the synthesis of these heptalenes should be the corresponding 1- and 2-aryl-substituted

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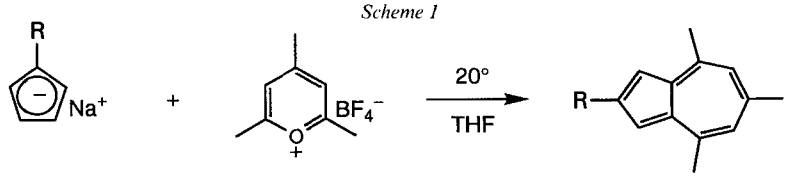
[2]) This is also true for the very first synthesis of *Pfau* and *Plattner* [3] which yielded *inter alia* 4-phenylazulene and served as proof for the structure of azulenes. Further syntheses of azulenes with aryl substituents at the five- as well as at the seven-membered ring have been performed by *Plattner et al.* [4] [5], *Pommer* [6], *Hafner* and *Kaiser* [7], *Nozoe et al.* [8] [9], *Yasumani et al.* [10] [11], *Gassman et al.* [12] [13], *Copland et al.* [14] as well as *Houk et al.* [15]. In a further variant, *Jutz* and *Schweiger* assembled the Ph and 1,1′-biphenyl-4-yl group directly at the skeleton of 6-methylazulene [16].

4,6,8-trimethylazulenes (see, *e.g.* [26]). There are, in principle, two established azulene syntheses that should lead to the desired compounds, namely the reaction of the corresponding aryl-substituted sodium cyclopentadienides with 2,4,6-trimethylpyrylium salts according to *Hafner* and *Kaiser* [7] or the [8+2] cycloaddition of 4,6,8-trimethyl-2*H*-cyclohepta[*b*]furan-2-one with the corresponding aryl-substituted enamines according to *Nozoe et al.* [8]. However, the reaction of sodium phenylcyclopentadienide (**1a**) in THF with 2,4,6-trimethylpyrylium tetrafluoroborate (**2**) gave only 4,6,8-trimethyl-2-phenylazulene (**3a**) in moderate yields (*Scheme 1*)[3]).

Scheme 1



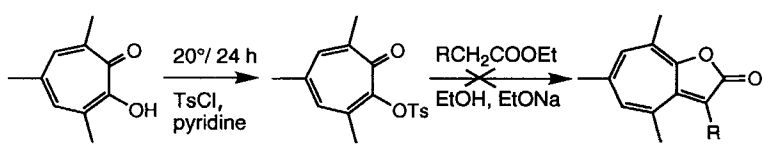
1a R = Ph
b R = 4-MeO–C_6H_4

2

3a R = Ph (15–20%)
b R = 4-MeO–C_6H_4

The synthesis of the corresponding sodium (4-methoxyphenyl)cyclopentadienide (**1b**) turned out to be much more difficult than that of **1a** and its reaction with **2** yielded only 3% of a mixture of 2- and 1-(4-methoxyphenyl)-4,6,8-trimethylazulene (**3a** and **4b**, respectively). The second approach *via* [8+2]-cycloaddition reactions was blocked already at its very beginning, since we were not able to condense 3,5,7-trimethyltropolone (**5**), which was accessible by hydroxymethylation and reduction of tropolone (*cf.* [29]), with AcOEt or $PhOH_2COOEt$, following the procedure of *Nozoe et al.* [30], to yield the corresponding 2*H*-cyclohepta[*b*]furan-2-ones **7** (*Scheme 2*)[4]).

Scheme 2



5

6 (75%)

7 (R = H, Ph)

Therefore, we searched for radical arylations of 4,6,8-trimethylazulene (**8**) which should mainly lead to substitution at C(1) of the azulenes according to earlier results of others authors (*cf.* [32–34]).

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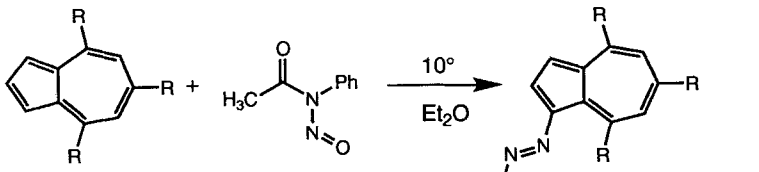
[3]) It has already been observed that the reaction of sodium methylcyclopentadienide in THF with 2,4,6-trimethylpyrylium perchlorate yields mainly 2,4,6,8-tetramethylazulene [7] [27], but that the reaction of sodium methoxycarbonylcyclopentadienide with 2,4,6-trimethylpyrylium tetrafluoroborate yields a mixture of methyl 4,6,8-trimethylazulene-1- and -2-carboxylate [28].

[4]) Indeed, **7** (R = H) has been prepared in 45–50% yield by vacuum flash pyrolysis (650°/10^{-4} Torr) of 2,4,6-trimethylphenyl propiolate [31].

2. Results and Discussions. – According to *Arnolds* and *Pahls* [32], azulene (**9**) can be phenylated in benzene or Et_2O solution at C(1) with *N*-nitroso-*N*-phenylacetamide (**10**). Later results of *Anderson* and *Chang* [33] showed, however, that the main product of this reaction is 1-(phenylazo)azulene (**11**), and 1-phenylazulene is only the minor product[5]). Indeed, when we repeated the reaction of **8** as well as of **9** with **10** in Et_2O solution, the only products that could be isolated were the corresponding 1-phenylazo compounds **11** and **12**, respectively (*Scheme 3*).

Scheme 3



a) 44% of **8** was recovered. b) 27% of **9** was recovered.

It seems that azulenes are too nucleophilic, so that they trap the phenyldiazonium ions which are in equilibrium with the phenyl diazoacetate formed from **10** (*cf.* [35]). *Nefedov et al.* [34] have shown, however, that azulene (**9**) can be arylated with aryl radicals which are generated from the corresponding arylhydrazines by oxidation with Cu^{II} ions in pyridine. Nowadays, this appears to be the most effective method for the radical arylation of azulene. However, the regioselectivity of the reaction is difficult to control, because substitution occurs at C(1), C(2), C(4), and C(6) with a clear predominance of C(1) (*cf.* [34]).

Scheme 4 delineates our results on the arylation reaction of 4,6,8-trimethylazulene (**8**) with phenylhydrazine (**13a**) and its *p*-methoxy and *p*-nitro derivative **13b** and **13c**, respectively.

As expected, the products **4**, which are aryl-substituted at C(1), clearly predominate. However, there is an obvious dependence of the yield of arylated products and the *p*-substituent in the phenyl hydrazine **13**. The best yield is obtained with the most electrophilic 4-nitrophenyl radical. On the other hand, the 4-methoxyphenyl radical shows the lowest yield of arylation. In addition to monoarylated products **3** and **4**, we also found small amounts of the diarylated products **14** and **15**, at least in the case where the Ar substituent is Ph and *p*-nitrophenyl. The precursor of **15a** can only be **4a**. The finding that the analogous diarylated product **15c** is not observed is in accordance with the fact that the *p*-nitrophenyl substituent in **4c** deactivates the azulene for a second attack of an electrophilic *p*-nitrophenyl radical. The source for the 1,2-diarylated azulenes **14a** and **14c** seems to be the 2-arylated azulenes **3a** and **3c** which carry the Ar substituent in the nodal plane of the corresponding HOMO, *i.e.*, an electron-attracting substituent at C(2) of the azulenes does not influence very much their reactivity against electrophilic radicals[6]).

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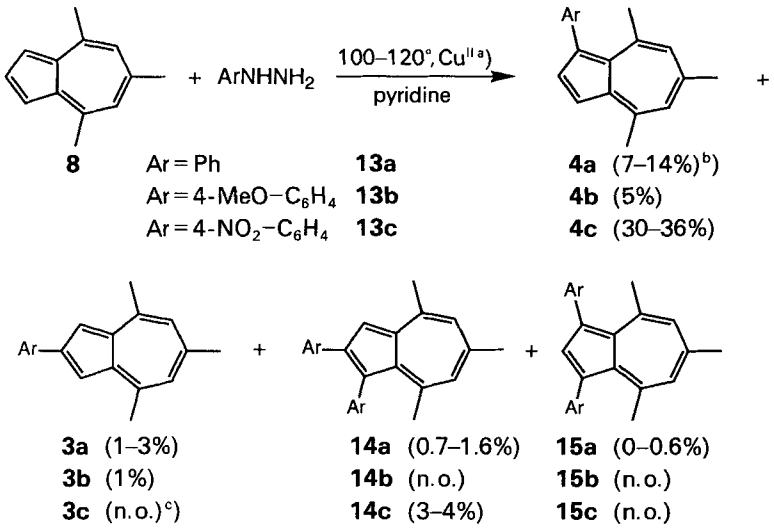
[5]) Similar results have been reported by *Nefedov et al.* [34].

[6]) *Nefedov et al.* [34] observed also the formation of 1,2-diphenylazulene in the arylation reaction of azulene (**9**).

Scheme 4



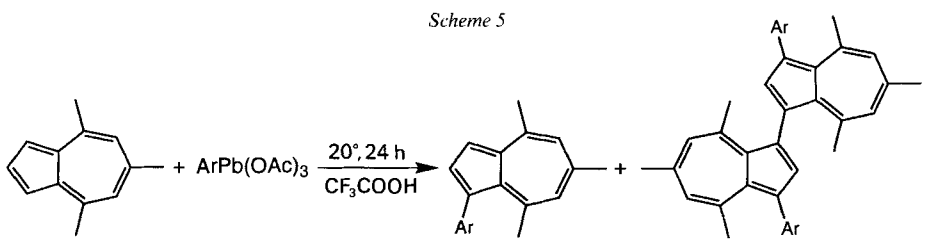
a) In total, a 1:1 mixture of $CuF_2 \cdot 2H_2O$ and $CuCO_3 \cdot Cu(OH)_2$ was applied in a 50% molar excess with respect to **13**. The molar ratio of **8** to **13** amounted to 1:10.

b) In parentheses are given the isolated yields as well as their range on the basis of several runs. In the *Exper. Part*, only the runs which gave the best yields are described. In all cases, 25–40% of **8** have been recovered.

c) n.o. = not observed.

Since the yield of 1-(4-methoxyphenyl)-4,6,8-trimethylazulene (**4b**) was low in the described arylation reaction, we looked for another type of aromatic arylation [36] of **8**. *Pinhey et al.* [37] [38] have shown that cationic arylation of aromatic compounds can be well performed with aryllead(IV) tricarboxylates [39] in CF_3COOH, especially when the aryl substituent carries π-donor groups such as MeO group. It is assumed that the arylation reactions take place *via* corresponding cationic π-complexes (*cf.* [37] [38]). Since it is well documented that azulenes easily form π-donor/acceptor complexes with π-acids such as picric acid or 1,3,5-trinitrobenzene (*cf.* [49]), we studied the reaction of (4-methoxyphenyl)lead(IV) triacetate (**16**) [41] with **8** in CF_3COOH (*Scheme 5*).

Scheme 5



a) 38% of **8** were recovered.

Indeed, azulene **4b** was formed in a yield of 43% with respect to reacted **8**, and it was not accompanied by its 2-substituted isomer **3b**. On the other hand, we could isolate the 1,1'-biazulene **17** in a yield of 6% with respect to reacted **8**[7]). We assume that **4b** is the precursor of **17**, and that it is formed by one-electron oxidation of **4b** by the 4-methoxyphenyl cation in the corresponding π-complex.

Radical dimerization of $\mathbf{4b}^{+\cdot}$ and loss of two protons from the dimer will directly yield **17** (see, however, the discussion in [43]). The results show that cationic arylations of azulenes with $ArPb(OAc)_3$ in CF_3COOH may become difficult at the moment where the oxidation potentials of starting azulenes or product azulenes are lower than that of $Ar^{\cdot}$ in $ArPb(OAc)_3$, so that the corresponding $(azulene)^{+\cdot}$ are formed in preference to the σ-complex of the starting azulene and Ar^+ in $ArPb(OAc)_3$ or the corresponding trifluoroacetate.

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Experimental Part

General. M.p. on a *Büchi* apparatus (model *FP5/52*). The values are not corrected. TLC on silica gel on aluminium foils (silica gel *60 F 254, Merck*; layer thickness 0.2 mm). Evaporation of solvents on a rotatory evaporator (r.e.) at 0–40° and 15 Torr. Column chromatography (CC) on a *Lobar®* column (310 × 25 mm; *LiChroprep®* Si: *60*; *Merck*) under medium pressure. UV Spectra on an *Otsuka* spectrophotometer (model *MCPD 1100*). Maxima and minima (λ_{max} and λ_{min}) in nm (log ε). IR Spectra on a *Perkin-Elmer* FT-IR spectrophotometer (model *FT-IR 1600*); band positions in cm^{-1}. ^{1}H-NMR Spectra at 300 MHz on a *Bruker* instrument (model *AC 300*). ^{13}C-NMR Spectra at 50 MHz on a *Varian* instrument (model *XL 200*). Chemical shifts with respect to TMS (= 0) as internal standard; Coupling constants *J* in Hz. MS on a *Finnigan* instrument (model *MAT SSQ 700*); EI at 70 eV; ions in *m/z* (rel. %).

1. *4,6,8-Trimethyl-2-phenylazulene* (**3a**). *Sodium phenylcyclopentadienide* (**1a**) was prepared from phenylcyclopentadiene (4.72 g, 33.20 mmol; preparation according to [44]) and Na suspension (0.7 g, 30.2 mmol) in THF (40 ml). After addition of 3.62 g (17.20 mmol) of *2,4,6-trimethylpyrylium tetrafluoroborate* (**2**; preparation according to [45]), a rise in temp. and spontaneous coloration to violet was observed. Stirring was continued for another 30 min, followed by removal of THF (r.e.). Usual workup (*cf.* [46]) provided 0.840 g (3.41 mmol, 20%) of **3a**. Violet crystals. M.p. 131.6–132.6° (hexane). R_f(hexane/Et_2O 9:1): 0.36. UV (hexane): λ_{max} 396 (4.09), 380 (4.06), 313 (4.81), 304 (4.79), 245 (4.31); λ_{min} 384 (4.05), 336 (3.70), 307 (4.85), 266 (4.00). IR (KBr): 2980*w*, 2920*w*, 1570*s*, 1560*s*, 1540*m*, 1520*w*, 1470*s*, 1440*s*,1370*w*, 1330*s*, 1220*s*, 1100*w*, 1070*w*, 1030*w*, 920*w*, 840*s*, 810*s*, 760*s*, 690*s*, 650*w*, 630*w*. ^{1}H-NMR ($CDCl_3$): 8.01–7.98 (*dd*-like, *J* = 8.5, 1.3, 2 arom. H); 7.65 (*s*, H–C(1,3)); 7.51–7.45 (*t*-like, *J* = 7.8, 2 arom. H); 7.38–7.32 (*t*-like, *J* = 7.3, 1 arom, H); 7.09 (*s*, H–C(5), H–C(7)); 2.93 (*s*, Me–C(4), Me–C(8)); 2.64 (*s*, Me–C(6)). CI-MS: 248 (15), 247 (100, $[M + 1]^+$). Anal. cal. for $C_{19}H_{18}$ (246.36): C 92.63, H 7.36; found: C 92.36, H 7.56.

2. *1-(Phenylazo)azulene* (**11**; *cf.* [32]). To a soln. of 0.250 g (1.95 mmol) *azulene* (**9**) in 5 ml Et_2O, 0.250 g (1.52 mmol) of N-*nitroso*-N-*phenylacetamide* (**10**; for preparation *cf.* [47]) was added at 0°. After 1 h, a change of color from violet to brown occurred. Another 10 ml of Et_2O were added, the org. phase was extracted with H_2O, dried (Na_2SO_4), and the org. phase evaporated (r.e.). CC (hexane/AcOEt 9:1) yielded in a first fraction 0.068 g (0.52 mmol, 27%) of unreacted **9** and in a second fraction 0.145 g (0.62 mmol, 32%) of **11** in brown needles. M.p. 121° (hexane; [48]: 120–121° (hexane)). R_f(hexane/Et_2O 7:3): 0.30. UV (hexane): λ_{max} 413 (4.46), 328 (4.19), 278 (4.28), 234 (4.35); λ_{min} 360 (3.96), 300 (4.09), 260 (4.11). IR (KBr): 1590*m*, 1570*m*, 1560*m*, 1540*w*, 1450*w*, 1380*s*, 1330*m*, 1270*m*, 1190*w*, 790*s*, 770*m*, 750*s*, 690*s*. ^{1}H-NMR ($CDCl_3$): 9.36 (*d*, *J* = 9.8, H–C(4)); 8.37 (*d*, *J* = 4.8,

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[7]) 1,1'-Biazulenes of type **17** have already been synthetized by *Ullmann* coupling [42a] as well as by Ni^0-catalyzed coupling reactions [42b] of 1-X-azulenes (X = I, Br).

H–C(2)); 8.34 (*d*, J = 9.8, H–C(8)); 8.02 (*dd*, J = 8,6, 1.4, 2 arom. H_o); 7.74 (*t*, J = 9.8, H–C(6)); 7.54 (*t*, J = 7.3, 2 arom. H_m); 7.46 (*m*, H–C(5)); 7.45 (*d*, J = 4.9, H–C(3)); 7.43 (*m*, 1 arom. H_p); 7.33 (*t*, J = 9.7, H–C(7)). ^{13}C-NMR ($CDCl_3$): 154.11 (*s*); 143.89 (*s*); 143.83 (*s*); 139.44 (*d*); 138.66 (*s*); 138.42 (*d*); 135.42 (*d*); 129.20 (*d*); 128.94 (*d*, 2 arom. CH); 126.49 (*d*); 126.45 (*d*); 125.20 (*d*); 122.18 (*d*, 2 arom. CH); 119.89 (*d*). CI-MS: 234 (16), 233 (100, $[M + 1]^+$), 232 (20). Anal. cal. for $C_{16}H_{12}N_2$ (232.29): C 82.73, H 5.21, N 12.06; found: C 82.58, H 5.39, N 11.94.

3. *4,6,8-Trimethyl-1-(phenylazo)azulene* (**12**). As described above for **11**, 0.194 g (1.14 mmol) of *4,6,8-trimethylazulene* (**8**) [46] were reacted with 0.146 g (0.89 mmol) of **9** in 5 ml of Et_2O. CC (hexane/AcOEt 9:1) after workup yielded 0.085 g (0.50 mmol, 44%) of **8** and 0.083 g (0.30 mmol, 26%) of **12** as a brown oil. R_f(hexane/Et_2O 7:3): 0.29. UV (hexane): λ_{max} 425 (4.40), 336 (4.15), 312 (4.18), 243.8 (4.38); λ_{min} 372 (3.92), 327 (4.15), 272 (4.00). IR (KBr): 1580*m*, 1560*w*, 1520*w*, 1490*m*, 1425*w*, 1370*s*, 1320*s*, 1300*s*, 1290*s*, 1210*m*, 1220*m*, 1190*m*, 1140*w*, 1110*w*, 1060*w*, 1020*w*, 850*w*, 800*m*, 760*m*, 720*m*, 680*m*. ^{1}H-NMR ($CDCl_3$): 8.17 (*d*, J = 4.7, H–C(2)); 7.89 (*d*-like, J = 8.2, 2 arom. H_o); 7.51 (*t*-like, J = 8.0, 2 arom. H_m); 7.38 (*t*-like, J = 7.3, 1 arom. H_p); 7.38 (*d*, J = 4.7, H–C(3)); 7.32 (*s*, H–C(5)); 7.21 (*s*, H–C(7)); 3.39 (*s*, Me–C(4)); 2.89 (*s*, Me–C(6)); 2.66 (*s*, Me–C(8)). ^{13}C-NMR ($CDCl_3$): 154.26 (*s*); 149.62 (*s*); 147.63 (s); 147.34 (*s*); 147.06 (*s*); 140.49 (*s*); 133.69 (*s*); 132.94 (*d*); 130.64 (*d*); 128.90 (*d*, 2 arom. CH); 128.56 (*d*); 122.27 (*d*, 2 arom. CH); 121.92 (*d*); 117.92 (*d*); 29.65 (*q*); 28.51 (*q*); 25.30 (*q*). CI-MS: 276 (15), 275 (100, $[M + 1]^+$), 274 (34).

4. *Arylations of* **8** (*cf.* [34]). 4.1. *With Phenylhydrazine* (**13a**). To a soln. of 2.0 g (14.5 mmol) $CuF_2 \cdot 2\ H_2O$ (*Fluka*) in 30 ml of pyridine, 6.6 g (29.8 mmol) of $CuCO_3 \cdot Cu(OH)_2$ (*Fluka*) were added. After evaporation of 1.5 ml of the solvent, 0.681 g (4.0 mmol) of **8** were added, and the mixture was heated to 100–120°, followed by dropwise addition of 2.16 g (20.0 mmol) of **13a** in 5 ml of pyridine during 20 min under vigorous stirring. Again, 3 ml of the solvent were distilled off, the mixture was cooled to r.t. and diluted with 10 ml of pyridine. Further 6.60 g (29.8 mmol) $CuCO_3 \cdot Cu(OH)_2$ and 2.16 g (20.0 mmol) of **13a** in 5 ml pyridine were added. After cooling, addition of 1.0 g (45.9 mmol) of $CuF_2 \cdot 2\ H_2O$ and complete evaporation (r.e.) of pyridine followed. The residue was dissolved in Et_2O, the Et_2O phase extracted with 1N HCl, $NaHCO_3$, and NaCl (sat. aq. solns.), and dried (Na_2SO_4). Evaporation of Et_2O and CC (hexane) yielded the following fractions in the order of elution: 0.231 g (1.36 mmol, 34%) of **8** (violet crystals), 0.139 g (0.56 mmol, 14%) of **4a** (blue solid), 0.029 g (0.12 mmol, 3%) of **3a** (violet crystals), 0.008 g (0.03 mmol, 0.6%) of **15a** (blue solid), and 0.021 g (0.06 mmol, 1.6%) of **14a** (blue-violet solid).

4,6,8-Trimethyl-1-phenylazulene (**4a**). M.p. 115.0° (hexane). R_f(hexane/Et_2O 9:1): 0.37. UV (hexane): λ_{max} 352 (3.96), 297 (4.81), 246 (4.65); λ_{min} 330 (3.76), 262 (4.14). ^{1}H-NMR ($CDCl_3$): 7.67 (*d*, J = 4.1, H–C(2)); 7.50–7.38 (*m*, 5 arom. H); 7.46 (*d*, J = 4.1, H–C(3)); 7.13 (*s*, H–C(5)); 7.04 (*s*, H–C(7)); 2.99 (*s*, Me–C(4)); 2.68 (*s*, Me–C(6)); 2.53 (*s*, Me–C(8)). ^{1}H-NOE ($CDCl_3$, 400 MHz): 2.99 (Me–C(4))→7.13 (*s*, H–C(5)), 7.46 (*m*, H–C(3)); 2.68 (Me–C(6))→7.04 (*s*, H–C(7)), 7.13 (*s*, H–C(5)); 2.53 (Me–C(8))→7.04 (*s*, H–C(7)). ^{13}C-NMR ($CDCl_3$): 147.40 (*s*); 146.10 (*s*); 145.18 (*s*); 142.18 (*s*); 137.17 (*s*); 136.31 (*d*); 132.68 (*s*); 131.28 (*s*); 130.54 (*d*, 2 arom. CH); 128.77 (*d*); 127.30 (*d*, 2 arom CH); 126.90 (*d*); 125.91 (*d*); 114.91 (*d*); 28.65 (*q*); 28.44 (*q*); 25.50 (*q*).

4,6,8-Trimethyl-1,3-diphenylazulene (**15a**). M.p. 167.0–168.0° (hexane). R_f (hexane): 0.24. UV (hexane): λ_{max} 380 (3.84), 358 (3.89), 307 (4.62), 251 (4.53); λ_{min} 370 (3.82), 344 (3.78), 275 (4.31). ^{1}H-NMR ($CDCl_3$): 7.59 (*s*, H–C(2)); 7.46–7.29 (*m*, 10 arom. H); 6.93 (*s*, H–C(5), H–C(7)); 2.59 (*s*, Me–C(6)); 2.47 (*s*, Me–C(4), Me–C(8)). EI-MS: 323 (20), 322 (100, M^+), 307 (6), 292 (7), 291 (8).

4,6,8-Trimethyl-1,2-diphenylazulene (**14a**). M.p. 129.0–130.0° (hexane). R_f (hexane): 0.22. UV/VIS (hexane): λ_{max} 555 (2.91), 371 (3.85), 310 (4.69), 251 (4.38); λ_{min} *ca.* 400 (2.5), 344 (3.67), 271 (4.06). ^{1}H-NMR ($CDCl_3$): 7.47 (*s*, H–C(3)); 7.25–7.15 (*m*, 10 arom. H); 7.04 (*s*, H–C(7)); 6.93 (*s*, H–C(5)); 2.90 (*s*, Me–C(4)); 2.57 (*s*, Me–C(6)); 2.33 (*s*, Me–C(8)). ^{1}H-NOE ($CDCl_3$, 400 MHz); 2.33 (Me–C(8))→7.04 (*s*, H–C(7)); 2.57 (Me–C(6))→7.04 (*s*, H–C(7)), 6.93 (*s*, H–C(5)). ^{13}C-NMR ($CDCl_3$): 147.59 (*s*); 146.83 (*s*); 145.57 (*s*); 145.17 (*s*); 140.96 (*s*); 138.13 (*s*); 136.15 (*s*); 133.03 (*s*); 131.94 (*d*, 2 arom. CH); 130.83 (*d*); 129.79 (*d*); 129.66 (*d*, 2 arom. CH); 127.77 (*d*, 2 arom. CH); 127.54 (*d*); 127.32 (*d*, 2 arom. CH); 126.37 (*d*); 126.20 (*d*); 115.69 (*d*); 28.71 (*q*); 28.41 (*q*); 25.53 (*q*). EI-MS: 323 (23), 322 (100, M^+), 307 (7), 306 (7), 292 (10), 291 (12).

4.2. *With 4-Nitrophenylhydrazine* (**13c**). As described above (*4.1*), 0.340 g (2.0 mmol) of **8**, 1.53 g (10 mmol) of **13c**, 0.678 g (5.0 mmol) of $CuF_2 \cdot H_2O$, and 3.32 g (15.0 mmol) of $CuCO_3 \cdot Cu(OH)_2$ were reacted in 15 ml of pyridine. Workup and CC (hexane) yielded the following fractions in the order of elution: 0.090 g (0.53 mmol, 26%) of **8**, 0.210 g (0.72 mmol, 36%) of **4c** (brown crystals), and 0.033 g (0.08 mmol, 4%) of **14c** (brown oil).

4,6,8-Trimethyl-1-(4-nitrophenyl)azulene (**4c**). M.p. 180.0–181.0° (hexane). R_f(hexane/Et_2O 9:1): 0.20. UV (hexane): λ_{max} 400 (3.63), 353 (3.59), 295 (4.23), 246 (4.12); λ_{min} 367 (3.38), 326 (3.56), 270 (3.78). IR (KBr): 1590*s*, 1560*m*, 1510*s*, 1480*m*, 1460*w*, 1440*m*, 1420*m*, 1390*w*, 1370*m*, 1340*s*, 1280*w*, 1270*w*, 1220*w*, 1200*w*, 1110*w*, 1100*m*, 1070*w*, 1030*w*, 920*w*, 850*s*, 790*m*, 760*m*, 730*m*, 710*w*, 700*m*. ^{1}H-NMR ($CDCl_3$): 8.25–7.54 (*AA'BB'*, J = 8.8,

4 arom. H); 7.59 (*d*, *J* = 4.1, H–C(2)); 7.39 (*d*, *J* = 4.1, H–C(3)); 7.16 (*s*, H–C(5)); 7.07 (*s*, H–C(7)); 2.94 (*s*, Me–C(4)); 2.65 (*s*, Me–C(6)); 2.47 (*s*, Me–C(8)). CI-MS: 294 (9), 293 (18), 292 (100, $[M + 1]^+$). Anal. calc. for $C_{19}H_{17}NO_2$ (291.35): C 78.33, H 5.88, N 4.81; found: C 78.54, H 6.00, N 4.81.

4,6,8-Trimethyl-1,2-bis(4-nitrophenyl)azulene (**14c**). R_f (hexane/Et_2O 7:3): 0.13. UV (Et_2O): λ_{max} 367 (4.40), 314 (4.64), 248 (4.50); λ_{min} 350 (4.39), 269 (4.36), 223 (4.39). ^{1}H-NMR ($CDCl_3$): 8.20 (*d*, *J* = 8.7, 2 arom. H); 8.09 (*d*, *J* = 8.8, 2 arom. H); 7.49 (*s*, H–C(3)); 7.45 (*d*, *J* = 8.7, 2 arom. H); 7.31 (*d*, *J* = 8.8, 2 arom. H); 7.21 (*s*, H–C(7)); 7.09 (*s*, H–C(5)); 2.96 (*s*, Me–C(4)); 2.66 (*s*, Me–C(6)); 2.35 (*s*, Me–C(8)). CI-MS: 416 (7), 415 (5), 414 (19), 413 (100, $[M + 1]^+$).

4.3. *With 4-Methoxyphenylhydrazine* (**13b**). The reaction of sodium 4-methoxycyclopentadienide, which was, in analogy to **1a**, only available in bad yields, with **2** in THF (see *1*) gave **3b** and **4b** in an amount of only 2 and 1%, respectively.

As described above (*4.1*), 0.340 g (2.0 mmol) **8** and 1.75 g (10.0 mmol) of **13b** were reacted in 15 ml of pyridine. Workup and CC (hexane/Et_2O 8:2) yielded in the order of elution: 0.140 g (0.82 mmol, 41%) of **8**, 0.015 g (0.05 mmol, 2.7%) of **4b** (blue-violet crystals), and 0.002 g (0.007 mmol, 0.4%) of **3b** (blue-violet solid).

2-(4-Methoxyphenyl)-4,6,8-trimethylazulene (**3b**). ^{1}H-NMR ($CDCl_3$): 7.91 (*d*, *J* = 8.8, 2 arom. H); 7.53 (*s*, H–C(1), H–C(3)); 7.05 (*s*, H–C(5), H–C(7)); 7.00 (*d*, *J* = 8.8, 2 arom. H); 3.88 (*s*, MeO); 2.89 (*s*, Me–C(4), Me–C(8)); 2.62 (*s*, Me–C(6)).

1-(4-Methoxyphenyl)-4,6,8-trimethylazulene (**4b**). M.p. 136.5–137.5° (hexane). R_f(hexane/Et_2O 7:3): 0.50. UV (hexane): λ_{max} 354 (3.95), 294 (4.80), 247 (4.62); λ_{min} 335 (3.84), 265 (4.13). IR (KBr): 3060*w*, 3020*w*, 2980*w*, 2950*w*, 2920*w*, 2820*w*, 1600*w*, 1570*s*, 1550*m*, 1520*s*, 1490*s*, 1450*m*, 1440*s*, 1420*s*, 1370*m*, 1330*w*, 1300*w*, 1280*s*, 1240*s*, 1180*m*, 1170*s*, 1110*w*, 1100*m*, 1060*w*, 1030*s*, 990*w*, 910*w*, 850*w*, 830*s*, 780*m*, 720*w*, 710*w*, 650*w*, 630*w*, 610*w*. ^{1}H-NMR ($CDCl_3$): 7.58 (*d*, *J* = 4.0, H–C(2)); 7.39 (*d*, *J* = 4.0, H–C(3)); 7.33 (*d*, *J* = 8.6, 2 arom. H); 7.05 (*s*, H–C(5)); 6.97 (*s*, H–C(7)); 6.96 (*d*, *J* = 8.6, 2 arom. H); 3.90 (*s*, MeO); 2.93 (*s*, Me–C(4)); 2.62 (*s*, Me–C(6)); 2.48 (*s*, Me–C(8)). ^{13}C-NMR ($CDCl_3$): 158.12 (*s*); 147.42 (*s*); 146.02 (*s*); 145.62 (*s*); 137.04 (*d*); 136.38 (*d*); 134.55 (*s*); 132.31 (*s*); 131.39 (*d*, 2 arom. CH); 128.66 (*d*); 128.66 (*d*); 126.74 (*d*); 114.82 (*d*); 112.81 (*d*, 2 arom. CH); 55.27 (*q*); 28.49 (*q*); 28.42 (*q*); 25.46 (*q*). CI-MS: 278 (21), 277 (100, $[M + 1]^+$). Anal. calc. for $C_{20}H_{20}O$ (276.38): C 86.92, H 7.29; found: C 86.63, H 7.33.

5. *Reaction of* **8** *with (4-Methoxyphenyl)lead Triacetate* (**16**) (*cf.* [38]). At r.t., 0.264 g (1.55 mmol) of **8** and 0.493 g (1.00 mmol) of **16** (prepared according to [41]) were stirred in 5 ml CH_3COOH for 24 h. After usual workup and CC (hexane/Et_2O 9:1), the following products were obtained (in the order of elution): 0.100 g (0.59 mmol, 38%) of **8**, 0.075 g (0.42 mmol, 27%) of **4b** (blue-violet crystals), and 0.033 g (0.06 mmol, 4%) of **17** (green solid).

3,3'-Bis(4-methoxyphenyl)-4,4',6,6',8,8'-hexamethyl-1,1'-biazulene (**17**). M.p. 222.1–222.7° (Et_2O/hexane). R_f (hexane/Et_2O 7:3): 0.27. UV (Et_2O): λ_{max} 382 (4.22), 359 (4.34), 296 (4.97), 253 (4.87); λ_{min} 372 (4.24), 347 (4.36), 271 (4.70), 229 (4.65). IR (KBr): 3000*w*, 2950*w*, 2920*w*, 2820*w*, 1610*w*, 1570*s*, 1550*w*, 1500*s*, 1430 (br. *m*), 1390*w*, 1370*w*, 1330*w*, 1300*w*, 1280*m*, 1240*s*, 1170*m*, 1120*w*, 1100*w*, 1090*w*, 1030*m*, 990*w*, 910*w*, 870*w*, 830*s*, 790*w*, 760*w*, 700*w*, 640*w*. ^{1}H-NMR ($CDCl_3$): 7.49 (*s*, H–C(2), H–C(2')); 7.35 (*d*, *J* = 8.8, 4 arom. H); 6.92 (*d*, *J* = 8.8, 4 arom. H); 6.84 (*s*, H–C(5), H–C(5')); 6.80 (*s*, H–C(7), H–C(7')); 3.87 (*s*, 2 MeO); 2.54 (*s*, Me–C(4), Me–C(4')); 2.48 (*s*, Me–C(6), Me–C(6')); 2.33 (*s*, Me–C(8), Me–C(8')). CI-MS: 554 (9), 553 (28), 552 (42), 551 (100, $[M + 1]^+$), 539 (5), 537 (5). Anal. calc. for $C_{40}H_{38}O_2$ (550.75): C 87.23, H 6.95; found: C 86.99, H 7.16.

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