Cycloaddition

DOI: 10.1002/ange.200501276

Approach to the Blues: A Highly Flexible Route to the Azulenes**

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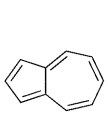
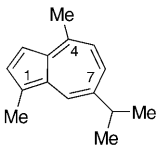
Dedicated to Dr. Jean-Louis Luche on the occasion of his retirement

Nearly a century and a half ago, Septimus Piesse applied the descriptive name azulene to azure-blue distillates from various sources, such as chamomile, yarrow, and wormwood.[1] However, it was only in 1937 that Placidus Plattner and Alexander Pfau successfully carried out the first synthesis of azulene (**1**),[2] the appellation given to the parent compound



Azulene (**1**)



Guaiazulene (**2**)

of the family of bicyclo[5.3.0]decapentaenes, which are now collectively referred to as the azulenes. Since this historical event, additional syntheses of the parent azulene and preparations of various other azulenes, such as guaiazulene (**2**), which is the archetype of the major azulene class, have been reported.[3] Although the approaches to these fascinating and electronically unique compounds are often ingenious, they suffer for the most part from being excessively long, low yielding, or lacking in generality. Many substitution patterns of the azulenes are still difficult to access, if they can be accessed at all.[3]

We have found that chlorotrienones **5a** and **5b** are readily prepared from cycloheptatriene and 7-methylcycloheptatriene, respectively, through a doubly regioselective cycloaddition of dichloroketene, a regioselective ring expansion with ethereal diazomethane, and dehydrochlorination in dimethylformamide (DMF; Scheme 1).[4]

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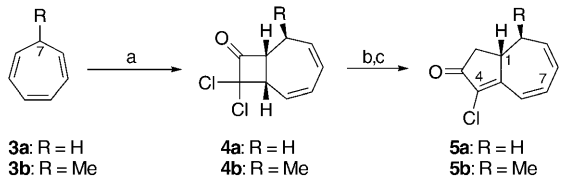
[**] We thank Prof. P. Dumy for his interest in our research, the Research Ministry for fellowship awards to S.C. and Y.C., and the Université Joseph Fourier and the CNRS (UMR 5616, FR 2607) for financial support.

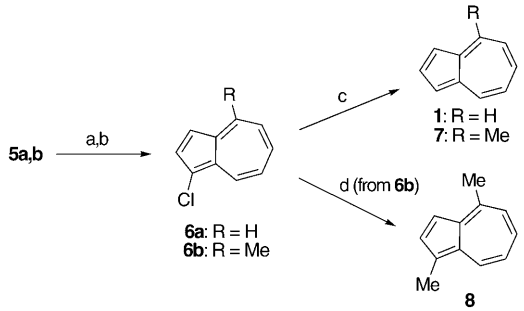


Scheme 1. Preparation of chlorotrienones **5a** and **5b**: a) Zn/Cu, $POCl_3$, CCl_3COCl, Et_2O, 20 °C, 20 h; b) CH_2N_2, MeOH/Et_2O (5:95), 0→20 °C, 35 min; c) DMF, 20 °C, 12 h (44–45 % yield, 3 steps).

As other C7-substituted cycloheptatrienes and diazoalkane reagents are also readily available[4a,5] for use in this sequence, it appeared to us that a broad approach to the azulenes might now be possible if 1) the oxygen atom at C3 could be excised, 2) the fused rings could be dehydrogenated to aromaticity, 3) the chlorine atom at C4 could be replaced, and 4) additional substituents could be regioselectively introduced into the trienones, particularly at C7. Herein, we disclose an efficient and exceptionally versatile preparation of azulenes, which are compounds of considerable interest for use in cosmetics,[6a] pharmaceutical preparations,[6b] and new molecular materials,[6c] through effective resolution of these concerns.

Azulene itself was targeted initially so that the first three critical points could be addressed at the outset. It was pleasing to find, after a number of failed attempts, that sequential treatment of **5a** with $NaBH_4/CeCl_3$, the Burgess reagent,[7] and *p*-chloranil could transform **5a** into chloroazulene **6a** in 45 % overall yield (Scheme 2).[8] Azulene could then be obtained from **6a** in 92 % yield through modification of the reduction recently described by Rahaim and Maleczkza.[9] Analogously, 4-methylazulene (**7**)[2,10] was readily prepared from **5b** in a slightly higher overall yield.

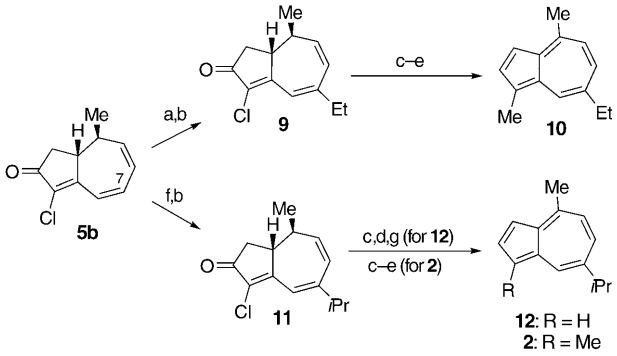
As most naturally occurring azulenes have methyl groups at C1 and C4, the discovery that **6b** could also be methylated by reaction with methylboronic acid, dpdb, and K_3PO_4[11] to give 1,4-dimethylazulene (**8**)[12a] in 98 % yield was welcomed



Scheme 2. Preparation of azulene (**1**), 4-methylazulene (**7**), and 1,4-dimethylazulene (**8**): a) $NaBH_4$, MeOH/$CeCl_3$, 0 °C, 1.5 h (from **5a**: 96 %; from **5b**: 98 %); b) the Burgess reagent, THF, 0→20 °C, 1 h; *p*-chloranil, 20 °C, 24 h (from **6a**: 47 %; from **6b**: 52 %); c) PMHS, $Pd(OAc)_2$, dpdb, K_3PO_4, THF, 80 °C, 12 h (**1**: 92 %; **7**: 91 %); d) $MeB(OH)_2$, $Pd(OAc)_2$, dpdb, K_3PO_4, PhMe, 100 °C, 24 h (98 %). Burgess reagent = (methoxycarbonylsulfamoyl)triethylammonium hydroxide inner salt, *p*-chloranil = tetrachloro-1,4-benzoquinone, PMHS = poly(methylhydrosiloxane), dpdb = dicyclohexylphosphano-2′,6′-dimethoxybiphenyl.

and augured well for the application of this approach to many other naturally occurring azulenes.[12b]

Considerable study was required to resolve point (4) satisfactorily. Although several different types of organometallic reagents did indeed add regio- (and stereo-)selectively to **5b** at C7, the yields were modest and, furthermore, aromatization of the resultant dienones proved difficult to achieve efficiently. We were, therefore, pleased to find that organozinc reagents, in the presence of CuOTf (cat.) and TMSCl,[13] were highly effective in transforming **5b** into the corresponding 1,6-conjugate addition products: Me, 91 %; Et, 98 %; *i*Pr, 71 %. Even better, it was discovered that simply by adding PhSeCl to the reaction mixture and then effecting oxidative (H_2O_2) elimination, the chlorotrienone system could be smoothly regenerated (Scheme 3).[14] Thus, chloro-

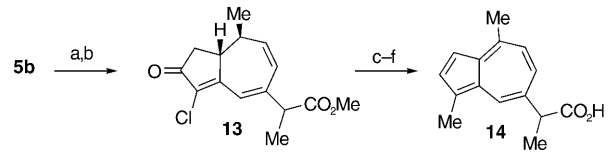


Scheme 3. Preparation of chamazulene (**10**), 7-isopropyl-4-methylazulene (**12**), and guaiazulene (**2**): a) 1. Et_2Zn, CuOTf, HMPA, TMSCl, −50 °C, 6 h; 2. PhSeCl, −50→0 °C, 2 h; b) H_2O_2, pyridine, 0 °C, 1 h (**9**: 71 %, 2 steps; **11**: 62 %, 2 steps); c) $NaBH_4$, MeOH/$CeCl_3$, 0 °C, 1.5 h (97 %); d) 1. Burgess reagent, THF, 0 °C, 1 h; 2. *p*-chloranil, 20 °C, 24 h (58–59 %); e) $MeB(OH)_2$, $Pd(OAc)_2$, dpdb, K_3PO_4, PhMe, 100 °C, 24 h (**10**: 89 %; **2**: 94 %); f) 1. iPr_2Zn, CuOTf, HMPA, TMSCl, −100 °C, 6 h; 2. PhSeCl, −50→0 °C, 2 h; g) PMHS, $Pd(OAc)_2$, dpdb, K_3PO_4, THF, 80 °C, 12 h (95 %). Tf = trifluoromethanesulfonyl, HMPA = hexamethylphosphoramide, TMSCl = trimethylsilyl chloride.

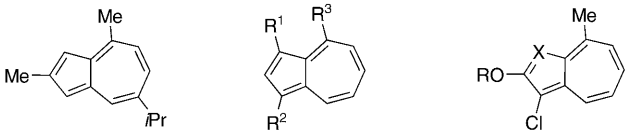
trienones **9** and **11** were prepared in 71 and 62 % yields, respectively. The former, through application of the above chemistry, provided chamazulene (**l0**), and the latter, 7-isopropyl-4-methylazulene (**12**) and guaiazulene (**2**).[15]

Ketene acetals can also be employed for 1,6-conjugate addition, thus adding to the synthetic possibilities: the treatment of **5b** with the *tert*-butyldimethylsilyl (TBDMS) ketene acetal, derived from methyl propionate, in the presence of lithium perchlorate[16] readily generated the 1,6-conjugate addition product, which on successive treatment with PhSeCl and H_2O_2 afforded chlorotrienone **13** (Scheme 4). Aromatization, methylation, and saponification then provided chamazulenecarboxylic acid (**14**).[17]

The attractiveness of the present approach resides, in part, in the diversity of structures that can readily be accessed with total regiocontrol, a feature that few other approaches enjoy. To further illustrate this point, regiochemically pure 7-isopropyl-2,4-dimethylazulene (**15**)[18a] (a naturally occurring isomer of guaiazulene (**2**)),[15b] 1-chloro-3-methylazulene (**16a**),[18b] and the phenylazulenes **16b**[18c] and **16c**[18d] have



Scheme 4. Preparation of (±)-chamazulenecarboxylic acid (**14**): a) 1. MeCH=C(OMe)OTBDMS, $LiClO_4$, CH_2Cl_2, 20 °C, 12 h; 2. PhSeCl, −50→0 °C, 2 h; b) H_2O_2, pyridine, 0 °C, 1 h (46%, 2 steps); c) $NaBH_4$, MeOH/$CeCl_3$, 0 °C, 1.5 h (92%); d) 1. Burgess reagent, THF, 0 °C, 1 h; 2. *p*-chloranil, 20 °C, 24 h (55%); e) $MeB(OH)_2$, $Pd(OAc)_2$, dpdb, K_3PO_4, PhMe, 100 °C, 24 h (99%); f) LiOH, THF, H_2O, 20 °C, 12 h (94%).



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16a: R^1 = Me, R^2 = Cl, R^3 = H
16b: R^1 = H, R^2 = Cl, R^3 = Ph
16c: R^1 = H, R^2 = Ph, R^3 = Me

17a: R = Ac, X = CH
17b: R = Me, X = N

also been efficiently prepared, thereby demonstrating four distinctly different substitution options as well. Finally, acetoxy and aza derivatives **17a**[18e] and **17b**[18f] are examples of novel azulenes that are readily prepared with this methodology.

In conclusion, modern chemistry has been applied to the long-standing problem of azulene synthesis and an efficient, highly flexible approach has resulted. Our approach allows controlled access to a wide variety of substituents and substitution arrays and should prove to be among the most broadly useful methods to prepare these important compounds.

Experimental Section

Experimental procedure for the preparation of **6b** from **5b**: $NaBH_4$ (43 mg, 1.13 mmol) was added to a stirred solution of **5b** (200 mg, 1.03 mmol) in MeOH/$CeCl_3$ (2.80 mL, 0.40 M, 1.12 mmol) at 0 °C. The reaction mixture was stirred for 1.5 h at 0 °C and then treated with a saturated solution of aqueous NaH_2PO_4. The crude product was isolated with EtOAc/pentane (1:1) in the usual manner and purified by column chromatography on dry silica gel with diethyl ether/pentane (40:60) to afford 198 mg (98%) of the *trans* alcohol as a white solid. M.p. 67–68 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (d, J = 7.1 Hz, 3H), 1.38–1.48 (m, 1H), 2.16–2.24 (m, 2H), 2.33 (pseudo q, $J\cong$7.3 Hz, 1H), 2.68–2.77 (m, 1H), 4.57 (pseudo t, $J\cong$7.2 Hz, 1H), 5.66 (dd, J = 11.4, 3.3 Hz, 1H), 5.85–5.94 (m, 1H), 6.01 (dd, J = 11.5, 6.9 Hz, 1H), 6.51 ppm (d, J = 11.5 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.2, 38.9, 40.3, 46.6, 74.6, 123.7, 125.3, 127.7, 133.6, 139.6, 141.5 ppm; FTIR: $\tilde{\nu}$ = 3360, 3016, 1700 cm^{-1}. A solution of the Burgess reagent (347 mg, 1.46 mmol) in dry THF (5 mL) was added to a stirred solution of the above alcohol (198 mg, 1.01 mmol) in dry THF (6.0 mL) at 0 °C. The reaction mixture was allowed to warm to 20 °C and stirred for 1 h, whereupon *p*-chloranil (745 mg, 3.03 mmol) was added and the resulting mixture was stirred for a further 24 h. The crude product was isolated with pentane in the usual way and purified by column chromatography on dry silica gel with pentane to give 92 mg (52%) of chloroazulene **6b** as a blue solid. M.p. 36 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.86 (s, 3H), 7.13 (d, J = 10.3 Hz, 1H), 7.14 (pseudo t (dd), $J\cong$9.5 Hz, 1H), 7.30 (d, J = 4.2 Hz, 1H), 7.53 (pseudo t (dd), $J\cong$10.3 Hz, 1H), 7.67 (d, J = 4.2, 1H), 8.40 ppm (d, J = 9.5 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 24.1, 113.4, 117.1, 122.0, 127.2, 133.3, 133.5, 134.8, 136.7, 137.8, 148.0 ppm; FTIR: $\tilde{\nu}$ = 3085, 3021, 2957, 2923, 2853, 1591, 1560, 1487, 1419, 1389, 1358, 906, 772, 743 cm^{-1}; MS (DCI): m/z: 177 $[M+H]^+$; HRMS calcd for $[C_{11}H_9Cl+H]^+$: 177.0471; found: 177.0484; elemental analysis (%) calcd for $C_{11}H_9Cl$: C 74.79, H 5.14; found: C 74.84, H 5.18.

Data for selected compounds: **2**: M.p. 31–32 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.36 (d, J = 6.9 Hz, 6H), 2.66 (s, 3H), 2.83 (s, 3H), 3.08 (sept, J = 6.9 Hz, 1H), 7.01 (d, J = 10.7 Hz, 1H), 7.22 (d, J = 3.7 Hz, 1H), 7.42 (dd, J = 10.7, 1.8 Hz, 1H), 7.62 (d, J = 3.7 Hz, 1H), 8.19 ppm (d, J = 1.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.0, 24.2, 24.9, 38.4, 112.9, 125.2, 125.3, 133.5, 135.0, 136.2, 136.4, 137.4, 140.0, 144.4 ppm; FTIR: $\tilde{\nu}$ = 3095, 3064, 2958, 2924, 2854, 1554, 1527, 1462, 1420, 1387, 1367, 772 cm^{-1}; MS (DCI): m/z: 199 $[M+H]^+$; HRMS calcd for $[C_{15}H_{19}+H]^+$: 199.1487; found: 199.1482.

10: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (t, J = 7.6 Hz, 3H), 2.65 (s, 3H), 2.82 (s, 3H), 2.83 (q, J = 7.6 Hz, 2H), 6.98 (d, J = 10.5 Hz, 1H), 7.21 (br s, 1H), 7.38 (dd, J = 10.5, 1.9 Hz, 1H), 7.61 (br s, 1H), 8.15 ppm (d, J = 1.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.0, 17.5, 24.2, 34.0, 112.9, 125.1, 125.2, 134.8, 135.9, 136.3, 136.4, 136.5, 137.5, 144.4 ppm; FTIR: $\tilde{\nu}$ = 3098, 3063, 2960, 2926, 2866, 1555, 1561, 1526, 1452, 1422, 1364, 772 cm^{-1}; MS (DCI): m/z: 185 $[M+H]^+$; HRMS calcd for $[C_{14}H_{16}+H]^+$: 185.1330; found: 185.1334; elemental analysis (%) calcd for $C_{14}H_{16}$: C 91.25, H 8.75; found: C 91.44, H 8.86.

12: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 (d, J = 6.8 Hz, 6H), 2.88 (s, 3H), 3.07 (sept, J = 6.8 Hz, 1H), 7.11 (d, J = 10.6 Hz, 1H), 7.29 (d, J = 3.8 Hz, 1H), 7.31 (d, J = 3.8 Hz, 1H), 7.46 (dd, J = 10.6, 2.0 Hz, 1H), 7.80 (pseudo t (dd), $J\cong$3.8 Hz, 1H), 8.31 ppm (d, J = 2.0 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 24.3, 24.7, 38.2, 114.7, 118.0, 126.0, 135.3, 135.4, 136.6, 137.4, 140.2, 141.8, 145.2 ppm; FTIR: $\tilde{\nu}$ = 3093, 3064, 2958, 2924, 1556, 1529, 1461, 1422, 1389, 1362, 749 cm^{-1}; MS (DCI): m/z: 185 $[M+H]^+$; HRMS calcd for $[C_{14}H_{16}]^+$: 184.1252; found: 184.1259.

14: M.p. 86–87 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61 (d, J = 7.2 Hz, 3H), 2.65 (s, 3H), 2.83 (s, 3H), 3.88 (q, J = 7.2 Hz, 1H), 7.00 (d, J = 10.7 Hz, 1H), 7.28 (d, J = 3.8 Hz, 1H), 7.44 (dd, J = 10.7, 1.9 Hz, 1H), 7.64 (d, J = 3.8 Hz, 1H), 8.22 ppm (d, J = 1.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.0, 19.2, 24.2, 48.8, 114.3, 125.1, 127.1, 130.9, 133.9, 135.7, 135.8, 136.9, 137.6, 145.6 ppm; FTIR: $\tilde{\nu}$ = 3585, 3103, 3065, 2961, 2923, 2853, 1704, 1556, 1454, 1261, 1023, 774 cm^{-1}; MS (DCI): m/z: 229 $[M+H]^+$.

Received: April 12, 2005
Published online: July 13, 2005

Keywords: aromatic compounds · azulenes · cycloaddition · natural products · synthesis design

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[18] a) Prepared by sequential treatment of **11** with MeMgBr, the Burgess reagent, *p*-chloranil, and PMHS/$Pd(OAc)_2$; b) synthesized by treatment of **4a** with $MeCHN_2$ rather than CH_2N_2, followed by DMF, $NaBH_4/CeCl_3$, the Burgess reagent, and *p*-chloranil; c) obtained from 7-phenylcycloheptatriene; see references [4a,5]; d) prepared from **6b** by using phenylboronic acid rather than methylboronic acid (98% yield); e) obtained by heating **5b** with Ac_2O and Pd/C in toluene (50% yield), for several related examples, see reference [4a]; f) synthesized from cyclobutanone **4b** by sequential treatment with *O*-mesitylenesulfonylhydroxylamine, $[Me_3O][BF_4]$, and DMF; for other examples of aza azulenes, see: M. Kitamura, S. Chiba, O. Saku, K. Narasaka, *Chem. Lett.* **2002**, 606 – 607.

