162. A Short Syntheses of 1,2-Dimethylazulenes

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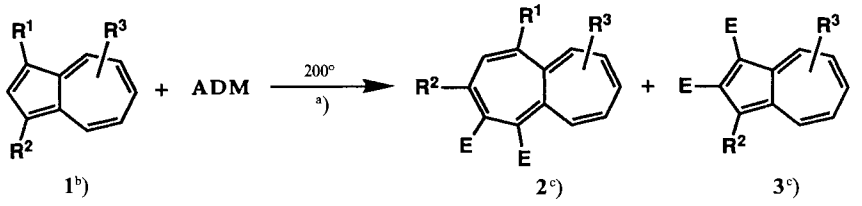
Dimethyl azulene-1,2-dicarboxylates are reduced with a 4–5 molar excess of DIBAH in Et_2O/hexane at 0° to yield the corresponding 2-(hydroxymethyl)-1-methylazulenes which can be further reduced to 1,2-dimethylazulenes on treatment with Et_3SiH in TFA at 60° (*cf.* the *Table*).

Introduction. – The thermal reaction of azulenes **1** with dimethyl acetylenedicarboxylate (ADM) in apolar solvents such as tetralin or decalin at 200° leads to the formation of heptalene-1,2-dicarboxylates **2** and azulene-1,2-dicarboxylates **3** in varying ratios, depending upon the substituents at the five-membered ring and the substitution pattern at the seven-membered ring in **1** (*cf.* [1–3], *Scheme 1*). In cases, where R^1 in **1** represents at *t*-Bu or a formyl group – both residues can easily be introduced into corresponding

Scheme 1



1[b]) **2**[c]) **3**[c])

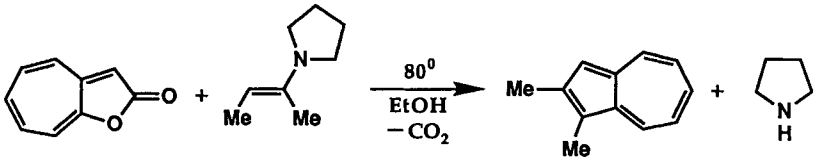
[a]) In tetralin or decalin. [b]) $R^1 = R^2$ = alkyl or R^1 = alkyl, formyl, R^2 = H. [c]) E = $COOCH_3$.

precursor azulenes by electrophilic substitution with *t*-BuOH/HBF_4 (*cf.* [4]) or DMF/$POCl_3$ (*Vilsmeier* formylation, *cf.* [5] as well as [1–3]) – the thermal reaction with ADM normally yields only the corresponding azulene-1,2-dicarboxylates **3** [6] (*cf.* [7]), *i.e.* azulenes with appropriate substituents at C(1) can easily be transformed into their corresponding 1,2-dicarboxylates by a cycloaddition/cycloreversion process (*cf.* [3] [8]). Therefore, azulene-1,2-dicarboxylates would be interesting starting materials for the synthesis of 1,2-dimethylazulenes, if the MeOCO groups at C(1), C(2) could efficiently be reduced to Me groups. Such a process would open the access to a whole variety of 1,2-dimethylazulenes.

To our knowledge, only the synthesis of 1,2-dimethylazulenes (**6**) itself has been achieved by a thermal [8 + 2] cycloaddition/cycloreversion sequence with the cycloheptafuranone **4** and a corresponding enamine **5** (*Scheme 2*) [9]. However, a generalization of

[1]) Part of the planned Ph.D. thesis of *R.A.F.*, University of Zurich.

Scheme 2

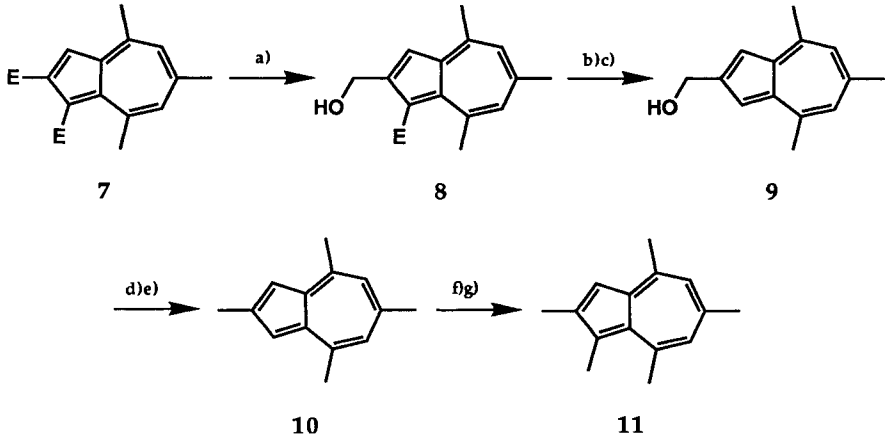


4 5 6

this method would be dependent on the synthetic accessibility of substituted 2*H*-cyclohepta[*b*]furan-2-ones **4** and their precursors, the corresponding tropolones, respectively (*cf.* [9] and literature cited there).

Results. – We have shown already that the MeOCO group at C(2) in dimethyl 4,6,8-trimethylazulene-1,2-dicarboxylate (**7**) can selectively be reduced to the CH_2OH group with DIBAH in THF/hexane to yield **8** (*Scheme 3*) [3]. In principle, following the reaction sequence shown in *Scheme 3* (*cf.* [3]), the ester group at C(1) in **8** can be saponified and the corresponding acid decarboxylated to yield the 2-(hydroxymethyl)-azulene **9** which opens the way to 2,4,6,8-tetramethylazulene (**10**) and, by applying standard procedures (*cf. Scheme 3* as well as [3]), also to 1,2,4,6,8-pentamethylazulene (**11**).

Scheme 3



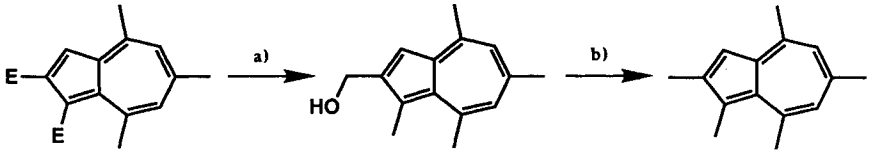
7 8 9

10 11

[a]) DIBAH, THF/hexane, −30 to −15°; 62%. [b]) KOH, EtOH/H_2O, 70°. [c]) 20% HCl; 85%. [d]) NCS/PPh_3, CH_2Cl_2. [e]) $NaBH_4$, DMSO, 20°; 66%. [f]) DMF/$POCl_3$; 90%. [g]) $NaBH_4/BF_3 \cdot Et_2O$, diglyme; 98%.

As we found now, the reaction sequence from **7** to **11** can appreciably be shortened, if **7** is reduced with a 3.5 molar excess of DIBAH in Et_2O/hexane at 0°. Under these conditions, **7** is directly reduced to the corresponding 2-(hydroxymethyl)-1,4,6,8-tetramethylazulene (**12**, *Scheme 4*). The reductive removal of the OH group in **12** could be realized by treatment of the latter with Et_3SiH in CF_3COOH at 60° (*cf.* [10]). The pentamethylazulene **11** was isolated in quantitative yield.

Scheme 4



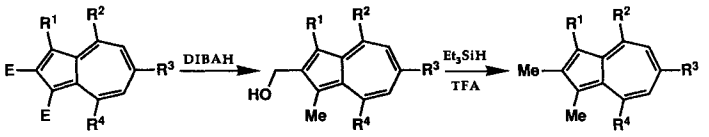
7 **12** **11**

[a]) DIBAH, Et_2O/hexane, 0°; 41% (not optimized). [b]) Et_3SiH, TFA, 60°/19 h; quant.

Further examples, collected in the *Table*, show that the described method can be generally applied for the reduction of azulene-1,2-dicarboxylates to the corresponding 1,2-dimethylazulenes. The transformation of dimethyl 3,6,8-trimethylazulene-1,2-dicarboxylates (**25**) into 1,2,3,4,6-pentamethylazulene (**27**) *via* the 2-(hydroxymethyl)azulene **26** demonstrates that a Me group at C(3) of the azulene-1,2-dicarboxylates do not hinder the reduction, *i.e.* also 1,2,3-trimethylazulenes are accessible by the described method.

That it is, indeed, the MeOCO group at C(2) that is reduced to the CH_2OH group follows from the fact that the CH_2 group in **14** (see the *Table*), when irradiated, induces

Table. *Two-Step Reduction of Dimethyl Azulene-1,2-dicarboxylates* **I** *to 1,2-Dimethylazulenes* **III** via *2-Hydroxy-1-methylazulenes* **II**[a])



I **II** **III**

Entry	R^1	R^2	R^3	R^4	**I**	DIBAH[b]) (molar excess)	**II**	Yield[c]) [%]	**III**	Yield [%]
1	H	Me	Me	Me	**7**	3.6	**12**	41	**11**	quant.
2	H	Me	*t*-Bu	Me	**13**	5	**14**	47	**15**	quant.
3	H	H	Me	H	**16**	12	**17**	55	**18**	quant.
4	H	Me	Me	H	**19**	7	**20**	92	**21**	quant.
5	H	H	Me	Me	**22**	11	**23**	63	**24**	99
6	Me	H	Me	Me	**25**	5	**26**	43	**27**	96

[a]) *Cf.* also *Scheme 4*. [b]) Calculated for 5 mol-equiv., necessary for the reduction of **I** to **II**. [c]) Yields of the first reduction step have not been optimized.

^{1}H-NOE on H–C(3) and Me–C(1) in the ^{1}H-NMR spectrum ((D$_6$)DMSO; *cf. Exper. Part*). In addition, the methylidene groups of all examples listed in the *Table* show nearly the same chemical shift ($\delta = 5.00 \pm 0.02$ ppm in $CDCl_3$; in **26** the CH_2 group resonates at 4.94 ppm).

Attempts to reduce the azulene-1,2-dicarboxylate **7** with $LiAlH_4$ in Et_2O or with sodium dihydridobis(2-methoxyethoxy)aluminate (SDMA) in toluene yielded complex reaction mixtures with the same TLC pattern. In both cases, small amounts of 1,2-bis-(hydroxymethyl)-4,6,8-trimethylazulene could be isolated which, on treatment with Et_3SiH/TFA, gave **11**. However, the described reduction with DIBAH in Et_2O/hexane followed by the second reduction with Et_3SiH/TFA gave much better results.

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Experimental Part

General. See [2] [3] [7] [8].

1. *1,2,4,6,8-Pentamethylazulene* (**11**; *cf.* [3]). 1.1. *2-(Hydroxymethyl)-1,4,6,8-tetramethylazulene* (**12**). *Dimethyl 4,6,8-trimethylazulene-1,2-dicarboxylate* (**7**; 0.645 g, 2.24 mmol) [2] was dissolved in Et_2O (60 ml) and cooled to 0°. At this temp., DIBAH in hexane (60 ml of a *ca.* 0.7M soln.; *ca.* 40 mmol) was slowly added. The blue colored soln. of **7** turned red at the beginning of the addition of DIBAH and became blue again at the end of the addition of DIBAH. The mixture was stirred for an additional h at 0°, and then AcOEt (60 ml) and H_2O (60 ml) were added dropwise. The inorg. salts were separated by filtration over *Celite*. The filtrate contained **12** which was purified by CC[2]). Recrystallization from hexane yielded pure **12** (0.191 g, 41%). Blue needles. M.p. 119–120°. R_f[3]) 0.23. UV (hexane): λ_{max} 357.0 (3.46), 341.9 (3.39), 295.3 (4.39), 289.8 (4.40), 247.2 (4.07); λ_{min} 345.4 (3.35), 322.7 (3.27), 293.3 (4.38), 262.3 (3.60). IR (KBr): 3420*s*, 2921*s*, 2854*m*, 1576*s*, 1516*m*, 1457*m*, 1422*m*, 1369*w*, 1310*s*, 1263*w*, 1086*s*, 1057*w*, 1006*s*, 836*s*, 800*s*. ^{1}H-NMR (300 MHz, $CDCl_3$/(D_6)DMSO): 7.36/7.26 (*s*, H–C(3)); 6.89/6.89 (*s*, H–C(5)); 6.88/6.87 (*s*, H–C(7)); 4.99/4.74 (*s*/*d*, $^3J(CH_2OH)$ = 5.4, CH_2OH); –/5.05 (*t*, $^3J(CH_2OH)$ = 5.4, CH_2OH); 3.02/2.95 (*s*, Me–C(8)); 2.80/2.72 (*s*, Me–C(6)); 2.78/2.65 (*s*, Me–C(4)); 2.54/2.50 (*s*, Me–C(1)). CI-MS (NH_3): 215 (100, $[M + 1]^+$).

1.2. *Reduction of* **12** *with Et_3SiH/TFA.* Compound **12** (0.195 g, 0.91 mmol) was dissolved in TFA (5 ml), and Et_3SiH (2 ml) was added. The mixture was stirred during 19 h at 60°. Eventually, the color of the soln. changed to brown. The mixture was poured on chopped ice and neutralized with powdered K_2CO_3 whereby the blue azulene color returned. The azulene **11** was extracted with Et_2O, and the combined etheral extracts were dried ($MgSO_4$). Azulene **11** was purified by CC to yield pure crystalline material (0.18 g, 100%). M.p. 61–64° ([3]: 66–69°). R_f 0.62. ^{1}H-NMR (300 MHz, $CDCl_3$; *cf.* [3]): 7.14 (*s*, H–C(3)); 6.84 (*s*, H–C(5,7)); 3.01 (*s*, Me–C(8)); 2.77 (*s*, Me–C(4)); 2.72 (*s*, Me–C(1)); 2.53 (*s*, Me–C(6)); 2.49 (*s*, Me–C(2)). ^{1}H-NOE (400 MHz, $CDCl_3$): 7.14 (H–C(3))→2.77 (*s*, Me–C(4)) and 2.49 (*w*, Me–C(2)); 3.01 (Me–C(8))→6.84 (*s*, H–C(7)) and 2.72 (*s*, Me–C(1)); 2.49 (Me–C(2))→7.14 (*w*, H–C(3)) and 2.72 (*s*, Me–C(1)).

2. *6-(*tert*-Butyl)-1,2,4,8-tetramethylazulene* (**15**). 2.1. *6-(*tert*-Butyl)-2-(hydroxymethyl)-1,4,8-trimethylazulene* (**14**). *Dimethyl 6-(*tert*-butyl)-4,8-dimethylazulene-1,2-dicarboxylate* (**13**; 0.525 g, 1.60 mmol) [11] was reduced with *ca.* 40 mmol of DIBAH in hexane (*cf. 1.1*). CC yielded **14** (0.191 g, 47%). Blue oil. R_f 0.23. IR (KBr): 3324*s*, 2954*s*, 2865*s*, 1572*s*, 1498*m*, 1451*m*, 1394*w*, 1359*m*, 1243*m*, 1200*m*, 1142*m*, 1087*m*, 993*s*, 848*m*, 806*m*. ^{1}H-NMR (300 MHz, $CDCl_3$/(D_6)DMSO): 7.30/7.24 (*s*, H–C(3)); 7.12/7.11 (*s*, H–C(5)); 7.11/7.08 (*s*, H–C(7)); –/5.06 (*t*, $^3J(CH_2OH)$ = 5.3, CH_2OH); 4.99/4.75 (*s*/*d*, $^3J(CH_2OH)$ = 5.3, CH_2OH); 3.07/3.01 (*s*, Me–C(8)); 2.85/2.78 (*s*, Me–C(4)); 2.78/2.65 (*s*, Me–C(1)); 1.43/1.39 (*s*, *t*-Bu). ^{1}H-NOE (400 MHz, (D_6)DMSO): 4.75 (CH_2OH)→7.24 (*s*, H–C(3)) and 2.65 (*s*, Me–C(1)); 3.01 (Me–C(8))→7.08 (*s*, H–C(7)) and 2.65 (*s*, Me–C(8)); 2.65 (Me–C(1))→4.75 (*s*, CH_2OH) and 3.01 (*s*, Me–C(8)).

2.2. *Reduction of* **14** *with Et_3SiH/TFA.* Compound **14** (0.100 g, 0.391 mmol) was dissolved in TFA (5 ml) and reduced with 2 ml of Et_3SiH at 60° (*cf. 1.2*). CC yielded pure **15** (0.093 g, 100%). Blue oil. R_f 0.62. UV (hexane): λ_{max} 355.7 (3.43), 341.3 (3.40), 295.3 (4.33), 290.5 (3.40), 247.3 (4.00); λ_{min} 347.4 (3.36), 334.0 (3.37), 291.2 (4.30), 261.1 (3.64). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.12 (*s*, H–C(3)); 7.08 (*s*, H–C(5,7)); 3.05 (*s*, Me–C(8)); 2.82 (*s*, Me–C(4)); 2.72 (*s*, Me–C(1)); 2.50 (*s*, Me–C(2)); 1.42 (*s*, *t*-Bu).

3. *1,2,6-Trimethylazulene* (**18**). 3.1. *2-(Hydroxymethyl)-1,6-dimethylazulene* (**17**). *Dimethyl 6-methylazulene-1,2-dicarboxylate* (**16**; 0.043 g, 0.17 mmol) [12] was reduced with *ca.* 10 mmol of DIBAH in hexane (*cf. 1.1*). CC yielded **17** (0.017 g, 55%). Viscous blue oil. R_f 0.24. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.08 (*d*, $^3J(8,7)$ = 10.4, H–C(8)); 8.07 (*d*, $^3J(4,5)$ = 10.0, H–C(4)); 7.28 (*s*, H–C(3)); 7.01 (*d*, $^3J(5,4) \approx 9.4$, H–C(5)[4]); 6.97 (*d*, $^3J(7,8) \approx 9.1$, H–C(7)); 5.03 (br. *s*, CH_2OH); 2.61 (s, Me–C(6)); 2.57 (*s*, Me–C(1)).

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[2]) Column chromatography (CC) on silica gel (230–400 mesh, ASTM) with Et_2O/hexane 1:1 (2-(hydroxymethyl)-1-methylazulenes) and Et_2O/hexane 1:4 (1,2-dimethylazulenes) as eluants.

[3]) TLC are on aluminium sheets, silica gel *60 F_{254} (Merck)*; layer thickness 0.2 mm. Moving phase for the 2-(hydroxymethyl)-1-methylazulenes: Et_2O/hexane 1:1 and for the 1,2-dimethylazulenes: Et_2O/hexane 1:4.

[4]) The *d* of H–C(5) and H–C(7) are superimposed to a *t*-like signal.

3.2. *Reduction of* **17** *with Et_3SiH/TFA.* Compound **17** (0.017 g, 0.91 mmol) was reduced in the usual manner (*cf. 1.2*) to yield after purification by CC **18** (0.015 g, 100%). Blue oil. R_f 0.65. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.99 (*d*, $^3J(8,7) = 10.0$, H–C(8)); 7.97 (*d*, $^3J(4.5) = 9.8$, H–C(4)); 7.09 (*s*, H–C(3)); 6.97 (*d*, $^3J(5,4) \sim 9.9$, H–C(5))[4]; 6.94 (*d*, $^3J(7,8) \approx 9.6$, H–C(7)); 2.59 (*s*, Me–C(1)); 2.54 (*s*, Me–C(6)); 2.51 (*s*, Me–C(2)).

4. *1,2,4,6-Tetramethylazulene* (**21**). 4.1. *2-(Hydroxymethyl)-1,4,6-trimethylazulene* (**20**). *Dimethyl 4,6-dimethylazulene-1,2-dicarboxylate* (**19**; 0.075 g, 0.276 mmol) [12] (*cf.* [3]) was reduced with *ca.* 10 mmol of DIBAH in hexane (*cf. 1.1*). Workup by CC yielded pure **20** (0.050 g, 92%). Viscous blue oil. R_f 0.24. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.10 (*d*, $^3J(8,7) = 9.85$, H–C(8)); 7.32 (*s*, H–C(3)); 7.01 (br. *s*, H–C(5)); 6.98 (*d* with f.s., $^3J(7,8) = 9.85$, H–C(7)); 5.03 (br. *s*, CH_2OH); 2.83 (*s*, Me–C(6)); 2.61 (*s*, Me–C(4)); 2.56 (*s*, Me–C(1)).

4.2. *Reduction of* **20** *with Et_3SiH/TFA.* Compound **20** (0.050 g, 0.092 mmol) was reduced in TFA (5 ml) with Et_3SiH (2 ml) at 60° (*cf. 1.2*). Purification by CC yielded pure **21** (0.045 g, 100%). Blue oil. R_f 0.63. UV (hexane): λ_{max} 357.4 (3.67), 340.5 (3.55), 311.2 (4.03), 295.4 (4.81), 286 (sh, 4.74), 241.3 (4.35), 204.2 (4.37); λ_{min} 346 (3.48), 328 (3.42), 258 (4.00), 224 (4.20). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.00 (*d*, $^3J(8,7) = 9.8$, H–C(8)); 7.26 (*s*, H–C(3))[5]; 6.97 (br. *s*, H–C(5)); 6.95 (*d*, $^3J(7,8) = 9.8$, H–C(7)); 2.80 (*s*, Me–C(6)); 2.59 (*s*, Me–C(4)); 2.54 (*s*, Me–C(1)); 2.51 (*s*, Me–C(2)).

5. *1,2,6,8-Tetramethylazulene* (**24**). 5.1. *2-(Hydroxymethyl)-1,6,8-trimethylazulene* (**23**). *Dimethyl 6,8-dimethylazulene-1,2-dicarboxylate* (**22**; 0.048 g, 0.176 mmol) [12] (*cf.* [3]) was reduced in the usual way with *ca.* 10 mmol of DIBAH in hexane (*cf. 1.1*). CC yielded pure **33** (0.022 g, 63%). Highly viscous blue oil. R_f 0.23. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.00 (*d*, $^3J(4,5) = 9.5$, H–C(4)); 7.21 (*s*, H–C(3)); 6.88 (br. *s*, H–C(7)); 6.83 (*d*, $^3J(5,4) = 9.5$, H–C(5)); 4.98 (br. *s*, CH_2OH); 3.02 (*s*, Me–C(8)); 2.79 (*s*, Me–C(6)); 2.54 (*s*, Me–C(1)).

5.2. *Reduction of* **23** *with Et_3Si/TFA.* Compound **23** (0.020 g, 0.10 mmol) was reduced with Et_3SiH (2 ml) in TFA (5 ml) at 60° (*cf. 1.2*). CC yielded pure **24** (0.018 g, 99%). Blue oil. R_f 0.63. UV (hexane): λ_{max} 357.0 (2.83), 336.5 (2.76), 292.8 (3.93), 284 (sh, 3.85), 243.3 (3.48); λ_{min} 346 (2.74), 332 (2.75), 260 (3.19), 228 (3.41). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.90 (*d*, $^3J(4,5) = 9.5$, H–C(4)); 7.04 (*s*, H–C(3)); 6.85 (br. *s*, H–C(7)); 6.82 (*d* with f.s., $^3J(5,4) = 9.5$, H–C(5)); 3.01 (*s*, Me–C(8)); 2.74 (*s*, Me–C(6)); 2.52 (*s*, Me–C(1)); 2.49 (*s*, Me–C(2)).

6. *1,2,3,4,6-Pentamethylazulene* (**27**). 6.1. *2-(Hydroxymethyl)-1,3,4,6-tetramethylazulene* (**26**). *Dimethyl 3,6,8-trimethylazulene-1,2-dicarboxylate* (**25**; 0.057 g, 0.199 mmol) [3] was reduced with *ca.* 10 mmol of DIBAH (*cf. 1.1*). Purification by CC yielded **26** (0.018 g, 43%). Viscous blue oil. R_f 0.25. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.98 (*d*, $^3J(4,5) = 10.2$, H–C(4)); 6.77 (br. *s*, H–C(7)); 6.75 (*d*, $^3J(5,4) = 10.2$, H–C(5)); 4.94 (br. *s*, CH_2OH); 3.00 (*s*, Me–C(8)); 2.87 (*s*, Me–C(6)); 2.58 (*s*, Me–C(1)); 2.51 (*s*, Me–C(3)).

6.2. *Reduction of* **26** *with EtSiH/TFA.* The usual reduction (*cf. 1.2*) of **26** (0.018 g, 0.085 mmol) yielded after chromatographic purification **27** (0.016 g, 96%). Blue oil. R_f 0.63. UV (hexane): λ_{max} 361.5 (3.06), 344.8 (2.99), 313 (sh, 3.40), 297.2 (4.02), 290 (sh, 4.03), 244.5 (3.62), 203.9 (3.74); λ_{min} 351 (2.96), 333 (2.94), 268 (3.39), 229 (3.51). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.90 (*d*, $^3J(8,7) = 10.2$, H–C(8)); 6.75 (br. *s*, C(5)); 6.73 (*d*, $^3J(7,8) = 10.2$, H–C(7)); 2.99 (*s*, Me–C(4)); 2.75 (*s*, Me–C(6)); 2.50 (*s*, Me–C(1)); 2.49 (*s*, Me–C(2)); 2.33 (*s*, Me–C(3)).

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[5]) Signal overlapping with that of $CHCl_3$.