178. Synthesis of Cycloproparenes *via* Aromatization of 7-Oxanorbornenes with Low-Valent Titanium

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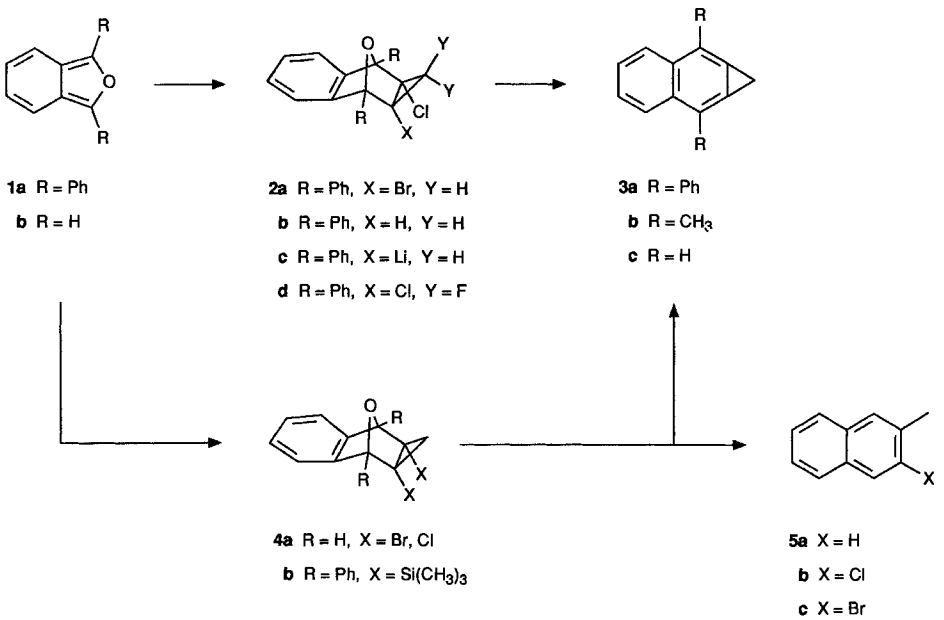
1*H*-Cyclopropa[*b*]naphthalene **3c** and the 2,7-diphenyl-substituted derivative **3a** have been synthesized *via* cycloaddition of the appropriate isobenzofurans **1a** and **1b** to 1-bromo-2-chlorocyclopropene and aromatization of the adducts with low-valent Ti. The same procedure afforded the 2,7-dimethyl-1*H*-cyclopropa[*g*]isoquinoline (**15**), but failed for the parent azacompound. Reaction of adducts of furans to 1-bromo-2-chlorocyclopropenes with low-valent Ti produced mixtures of cyclopropabenzenes **19** and 1,6-dihalogeno-1,3,5-cycloheptatrienes **18**. The latter could be converted to cyclopropabenzenes with BuLi.

Introduction. – The most general and most convenient syntheses of cycloproparenes involve base-induced aromatization of 1,1- or 2,7-dihalogeno-bicyclo[4.1.0]hept-3-enes [1][2]. For the so far only little known heterocyclic cycloproparenes [3][4], we have explored a variant of the bicyclo[4.1.0]hept-3-ene approach, consisting of cycloaddition of furans or isobenzofurans [5][6] to 1-bromo-2-chlorocyclopropene [7] and aromatization of the adducts. The feasibility of this procedure was examined in model studies which, ultimately, led to a simple access of 2,7-diphenyl-1*H*-cyclopropa[*b*]naphthalene [8] and of a substituted cyclopropaisoquinoline [9]. Some of the results of this study have already been reported in a preliminary form. This communication contains the experimental details and, in addition, further studies related to the aromatization of cycloadducts of furans to cyclopropenes.

Results and Discussion. – *Aromatization of Adducts of Isobenzofuran.* The aromatization of adducts of dihalogeno-cyclopropenes to furans or isobenzofurans can formally be effected by twofold metallation at the halogen substituents followed by β-elimination of the O-bridge. However, we found that these cycloadducts are very resistant towards aromatization. Typically, when the adduct **2a** (1-bromo-2-chlorocyclopropene to diphenylisobenzofuran **1a**) was reacted with BuLi, only reduction of the Br substituent to the hydrocarbon **2b** occurred, and the presumed intermediate organo-Li derivative **2c** did not undergo β-elimination (*Scheme 1*). We reasoned that the system needed some activation at the O-bridge, and in our search for a reagent which simultaneously attacks at the halogen and at the O-atom, we exploited the observation, that low-valent Ti [10] efficiently deoxygenates endoxides to arenes [11] and also reduces vicinal dihalides to alkenes [12]. Indeed, this reagent, prepared from $TiCl_3/LiAlH_4$ [10], converted adduct **2a** to 2,7-diphenyl-1*H*-cyclopropa[*b*]naphthalene (**3a**) in a yield of 72% in one step.

The structure of **3a** was established by the ^{1}H- and ^{13}C-NMR spectra: the protons of the cyclopropene resonate at 3.55 ppm, while the signal for C(1) appears at 19.95 ppm. The signals for C(2,7) are shifted strongly upfield to 122.6 ppm in the area typical for cycloproparenes. For example, the signals of C(2,7) of 2,7-dimethyl-1*H*-cyclopropa[*b*]naphthalene (**3b**) are found at 117.9 ppm [13] and those of C(2,5) in 2,5-diphenylbenzocyclopropene at 121.5 ppm [14].

Scheme 1

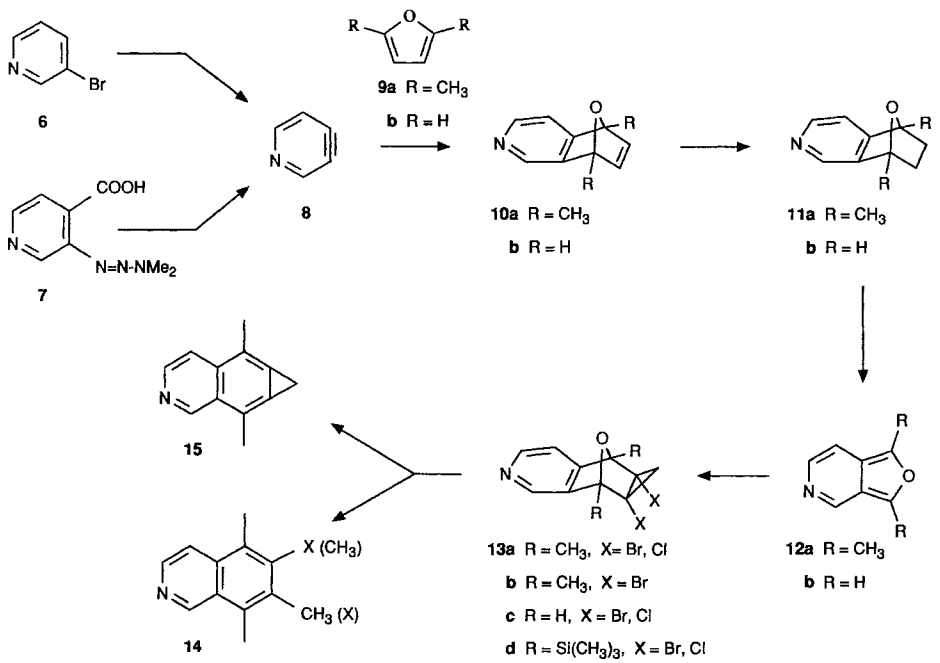


The presence of the Ph substituent at the bridgehead positions of the adduct **2a** is important for the success of the reaction. Thus, adduct **4a** of isobenzofuran (**1b**) [15] [16] to 1-bromo-2-chlorocyclopropene, under the same reaction conditions, afforded a 1:3 mixture of cyclopropa[*b*]naphthalene (**3c**) [17] and 2-methyl- (**5a**) and 2-chloro-3-methylnaphthalenes (**5b**) in 60% yield (combined). When the reaction time was shortened from 18 to 2 h, 2-bromo-3-methylnaphthalene (**5c**) was also observed. Since low-valent Ti usually does not attack aromatic chlorides [18], this suggests that the 2-methylnaphthalene is formed from **4a** directly *via* opening of the cyclopropane ring, rather than from **3c**. With $TiCl_3$/BuLi, the ratio of cyclopropa[*b*]naphthalene (**3c**) to methylnaphthalenes **5** improved to 3:1, but the best results were obtained with the low-valent Ti prepared from $TiCl_3$/MeLi. In this case, **3c** was formed in 60% yield and without contamination by methylnaphthalenes.

As an alternative approach to cycloproparenes, aromatization of adduct **4b** of 1,2-bis(trimethylsilyl)cyclopropene to isobenzofuran (**1b**), first described by *Halton* and coworkers [6], was attempted using F^- ions in conjunction of various reagents capable of coordination with the bridging O-atom. Invariably, either the starting material was recovered unchanged, or total decomposition occurred. Similar negative results have been obtained by *Halton* [19]. The cycloadduct **2d** [5] of **1** and 1,2-dichloro-3,3-difluorocyclopropene afforded no identifiable products upon exposure to low-valent Ti.

Synthesis of 2,7-Dimethyl-1H-cyclopropa[g]isoquinoline (**15**; *Scheme 2*). The aromatization can be applied to the heterocyclic precursor **13a**, which is available according to literature procedures: 3,4-dehydropyridine (**8**), obtained either by dehydrobromination of 3-bromopyridine (**6**) [20] or from 3-(3,3-dimethyltriazen-1-yl)pyridine-4-carboxylic acid (**7**) *via* pyrolysis [21], was trapped with 2,5-dimethylfuran (**9a**). The adduct **10a** was subjected to catalytic hydrogenation and the reduced material **11a** subjected to flash pyrolysis [22] at 600° to furnish the furopyridine **12a**, which was trapped *in situ* with 1-bromo-2-chlorocyclopropene to give a mixture of two isomeric adducts **13a**, differing in the position of the Br and Cl substituent with respect to the heteroatom, which were not separated. *Exo* addition of the cyclopropene to **12a** is attributed, on the grounds of the chemical shift of the H–C(1), *syn* to the O-bridge [5].

Scheme 2

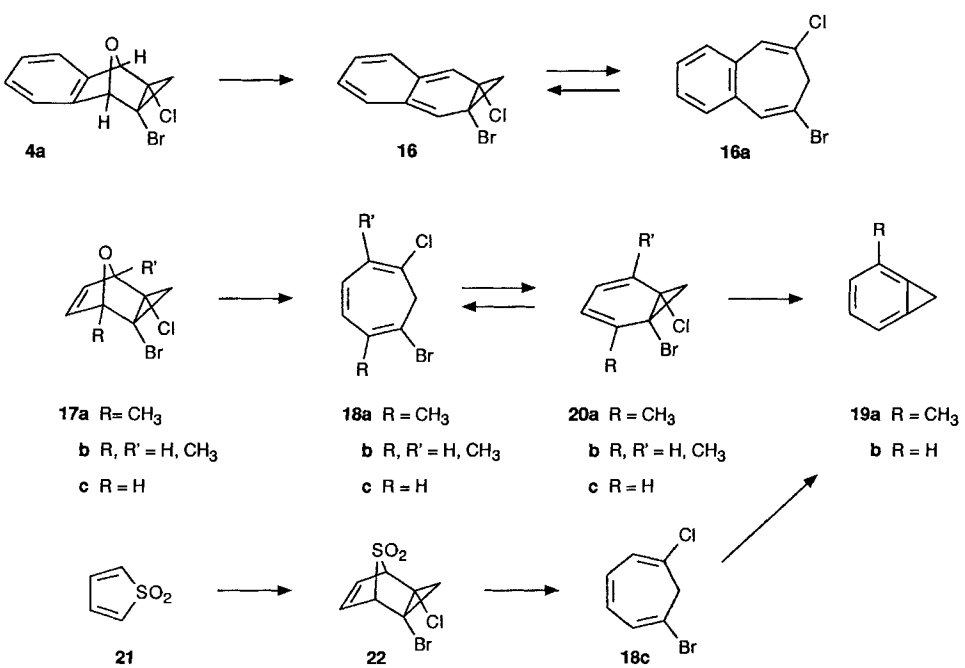


The aromatization of **13a** with low-valent Ti proved to be much more delicate than expected on the grounds of the model studies with **2a**. With $TiCl_3/LiAlH_4$, only decomposition products together with a 2- or 3-chloro-1,3 (2),4-trimethylisoquinoline **14** were formed. Total decomposition occurred, when MeLi/$TiCl_3$ 3:1 was used. With BuLi/$TiCl_3$ 2:1, the desired compound **15** was formed in 15% yield (after recrystallization from pentane), while other proportions of BuLi did not lead to product formation. We hoped to improve the reaction by replacement of the Cl by a Br substituent in **13a**; therefore, **12a** was intercepted with 1,2-dibromocyclopropene [6], but when the adduct **13b** was treated under the usual conditions, the results were similar to those obtained with **13a**.

Trapping of 3,4-dehydropyridine [21] with furan (**9b**) afforded the adduct **10b** in *ca.* 40% yield. After catalytic hydrogenation and flash pyrolysis (see above), the heterocyclic isobenzofuran **12b** was characterized by ^{1}H-NMR and then trapped at –20° with 1-bromo-2-chlorocyclopropene to afford the expected 1:1 mixture of isomers **13c** in 95% yield (with respect to sublimed **11b**). A large variety of aromatization methods were tried on **13c**, all based on low-valent Ti, but all led to decomposition of the starting material. Since aromatization of **13a**, which is substituted at the bridgehead positions leads to the desired product **15** albeit in poor yield, we speculated that silylation of these positions might overcome the difficulties experienced with **13c**. In analogy to a published procedure [23], **12b** was bis-silylated before trapping with the cyclopropene. The adduct **13d** underwent partial desilylation during chromatography and, when exposed to $TiCl_3$/BuLi, afforded no cycloproparene.

Aromatization of Adducts to Furans. Since the mechanism of the reaction of low-valent Ti, including the structure of the active Ti compound [24], is only poorly understood and subject to speculation, it seems premature to discuss the results reported above in mechanistic terms. Clearly, the fact that BuLi alone does not lead to aromatization suggests that the reaction must also involve the O-bridge. On the other hand, attack at the O-atom alone would not lead to the observed cycloproparenes but, instead, to bicycloheptadienes annellated with an *o*-quinoid benzene **16**, in equilibrium with the respective benzocycloheptatriene **16a** (*Scheme 3*).

Scheme 3



Since such *o*-quinoid structures are of high energy, their formation is unfavorable, and the pathway leading to cycloproparenes is favored. With adducts of 1-bromo-2-chlorocyclopropene to furans, the situation is different, because the intermediate bicycloheptadienes **20** have no *o*-quinoid structure and can form readily. In this case, the pathway involving only attack at the O-atom and leading to 1,6-dihalogeno-cycloheptatrienes **18** becomes competitive. Typically, the adduct **17a** of 2,5-dimethylfuran (**9a**) afforded only 2,7-dihalogeno-3,6-dimethylcycloheptatriene **18a** (30%). With **17b**, obtained from 2-methylfuran, a 1:1 mixture of the cycloproparene **19a** [25] and cycloheptatriene **18b** was produced. The product composition changed slightly, when more $LiAlH_4/TiCl_3$ was added to the reaction mixture, suggesting slow and incomplete conversion of 2,6-dihalogeno-cycloheptatriene **18b** to cycloproparene **19a**. This transformation appears to be feasible, because the cycloheptatriene can be in equilibrium with the norcaradiene **20b** [26], which allows the required 1,2-orientation of the halogens to be eliminated. However, in the past no cycloproparenes have been prepared by this procedure, except for cases where molecules were locked in the norcaradiene structure by incorporating them in a polycyclic system [27]. To verify this hypothesis, 2-bromo-6-chlorocycloheptatriene (**18c**) was independently synthesized *via* cycloaddition of 1-bromo-2-chlorocyclopropene to thiophene dioxide (**21**) [28] and extrusion of SO_2 from the adduct **22.** This is not a preparatively useful reaction, since the yield of **18c** is very poor; however, it has the advantage of providing access to dihalogeno-cycloheptatrienes without passing to the often undesirable cycloproparenes [29]. Exposure to $LiAlH_4/TiCl_3$ led to an 11% yield of cyclopropabenzene, analyzed *via* conversion to benzyl alcohol in presence of H_2O/Ag^+ [30]. The yield improved to 50%, when **18c** was reacted with BuLi.

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Experimental Part

General. The purity of the compounds was verified by TLC with plastic plates, covered with silica gel *60* F_{254} (*Merck*). The spots were located by a UV lamp (254 and 366 nm) and by treatment with phosphomolybdic acid (5%) in EtOH. Separation and purification of the compounds was effected by CC with silica gel *60*, 230–400 mesh. GC was carried out on a *Perkin Elmer 990* instrument with thermal conductivity detector with He as carrier. UV spectra were recorded on a *UVIKON 820* spectrometer with 1-cm quartz cell. The intensities are expressed in nm and the absorption coefficient as log ε. IR spectra are recorded on *Perkin Elmer 681* and *Polaris* FTIR spectrometers in soln. with NaCl cells or with KBr pellets.The absorptions are given in wave numbers (cm^{-1}). ^{1}H-NMR spectra were recorded at 60 MHz (*Varian EM-360, Varian T-60*), 200 MHz (*Varian XL-200*), or 360 MHz (*Bruker WH-360*). Chemical shifts (δ) are in ppm relative to TMS. ^{13}C-NMR at 50 MHz on a *Varian XL-200* instrument with ^{1}H decoupling. The substitution patterns of the various C-atoms were determined by an APT pulse sequence and are indicated in parentheses. ^{19}F-NMR spectra were recorded at 188 MHz (*Varian XL-200*). Chemical shifts (δ) are indicated relative to hexafluorobenzene ($\delta = 0$). Mass spectra were measured on *Varian EM-60, Finnigan 4000,* and *VG 70-70* instruments. The peaks corresponding to the ions of the mass *m/e* are given with relative intensities with respect to the base peak (100%).

Aromatization of Cyclopropene Adducts to 1,3-Diphenylisobenzofuran (1a) and Isobenzofuran (1b). – *1a*-endo-*Bromo-7a*-endo-*chloro-2,7-epoxy-1a,2,7,7a-tetrahydro-2,7-diphenylcyclopropa[b]-naphthalene* (**2a**). At –40° and under N_2, 1-bromo-2,2-dichloro-1-(trimethylsilyl)cyclopropane (0.5 g, mmol) in THF (15 ml) was added to Bu_4NF (1.0 g, 3.2 mmol) in THF (20 ml). The temp. was allowed to reach –20°, where the soln. was stirred for 1 h. Diphenylisobenzofuran (**1a**; 0.50 g, 1.6 mmol) was added in THF (20 ml),

and the mixture was stirred overnight at r.t. The solvent was evaporated and the residue dissolved with CH_2Cl_2 (100 ml). After washing with H_2O (2 × 50 ml) and drying ($MgSO_4$), the org. phase was evaporated. The crude product (930 mg) was recrystallized (EtOH). Yield 730 mg (85%) of **2a**. M.p. 149–150°. IR ($CHCl_3$): 3070*m*, 3040*m*, 1610*w*, 1500*m*, 1460*m*, 1450*m*, 1410*w*, 1350*m*, 1300*w*, 980*s*, 960*m*, 890*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.84 (*m*, 4 H); 7.50 (*m*, 6 H); 7.35 (*m*, 4 H); 2.69 (*AB*, $^2J_{AB}$ = 7, δ_A = 3.20, δ_B = 2.18). MS: 426, 424, 422 (M^+), 387 (3), 343 (8), 307 (6), 238 (5), 202 (26), 105 (100), 77 (71), 51 (20).

Reaction of **2a** *with BuLi. 1a*-endo-*Chloro-2,7-epoxy-1a,2,7,7a-tetrahydro-2,7-diphenyl-1*H-*cyclopropa[*b*]naphthalene* (**2d**). Compound **2a** (100 mg, 0.24 mmol) was reacted in THF (50 ml) at –78° with BuLi (0.35 ml, 1.4M; 0.5 mmol), and the mixture was allowed to warm up to r.t. overnight. The solvent was evaporated, the residue (75 mg) purified by CC (SiO_2, hexane/CH_2Cl_2 2:1) and gave **2d** (25 mg, 30%) as only identifiable product. IR ($CHCl_3$): 3079*w*, 3040*w*, 3010*m*, 1500*w*, 1458*m*, 1450*m*, 1355*m*, 1308*s*, 1240*m*, 1062*m*, 1020*m*, 1000*w*, 980*m*, 900*w*, 698*s*, 680*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.87 (*m*, 2 H); 7.86 (*m*, 2 H); 7.58–7.05 (*m*, 10 H); 2.18 (*ABC*, $^3J_{AB}$ = 384, $^3J_{AC}$ = 6.03, $^3J_{BC}$ = 7.62, δ_A = 2.50, δ_B = 2.07, δ_C = 1.83, 3 H). MS: 344 (2, M^+), 309 (15), 291 (10), 231 (15), 203 (24), 202 (33), 105 (100), 91 (5), 77 (85), 51 (23).

*2,7-Diphenyl-1*H-*cyclopropa[*b*]naphthalene* (**3a**). $TiCl_3$ (334 mg, 2.8 mmol) and $LiAlH_4$ (57 mg, 1.5 mmol) in THF (25 ml) were stirred under N_2 at r.t. for 30 min, then **2a** (200 mg, 0.28 mmol) in THF (10 ml) was added, and the mixture was stirred over night. It was decomposed with H_2O (20 ml) and extracted with Et_2O (2 × 50 ml). The combined org. layers were washed with sat. NaCl, dried ($MgSO_4$), and evaporated. The residue (200 mg) was purified by CC (SiO_2, hexane/CH_2Cl_2 2:1) and gave **3a** (100 mg, 72%). M.p. 131° (dec.). UV (hexane): 315 (4.39), 232 (3.85), 203 (3.76). IR ($CHCl_3$): 3085*m*, 3065*m*, 3015*m*, 3010*w*, 2950*m*, 1675*m*, 1575*w*, 1548*s*, 1530*w*, 1492*w*, 1448*s*, 1350*s*, 1105*m*, 1075*m*, 1030*m*, 1000*w*, 964*s*, 918*w*, 700 v. *s*, 638*s*, 630*m*, 615*s*. ^{1}H-NMR (CD_2Cl_2, 200 MHz): 8.2 (*m*, 2 H); 7.8–7.3 (*m*, 12 H); 3.58 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 137.9 (C); 135.6 (C); 130.2 (CH); 128.6 (CH); 127.6 (CH); 126.4 (CH); 125.7 (C); 125.5 (CH); 122.6 (C); 19.95 (CH_2) MS: calc. for $C_{23}H_{16}$: 292.1252, found: 292.12245; 292 (60, M^+), 291 (88), 289 (80), 276 (17), 263 (7), 215 (62), 145 (100), 138 (49), 132 (42), 119 (14), 77 (10), 63 (13), 51 (20).

1a-endo-*Bromo-7a*-endo-*chloro-2,7-epoxy-1a,2,7,7a-tetrahydro-1*H-*cyclopropa[*b*]naphthalene* (**4a**). To BuLi (2.2 ml, 1.6M; 3.5 mmol) in hexane at 0° under N_2, a soln. of $(i\text{-}Pr)_2NH$ (0.43 ml, 6 mmol) in benzene (1.25 ml) was added. The temp. was raised to 25°, and 1-methoxy- or 1-ethoxy-1,4-dihydroisobenzofuran (1.30 mmol) in benzene (2 ml) was added [15][16]. After stirring for 10 min, aq. NH_4Cl (10 ml) was added. The org. layer was separated and dried ($MgSO_4$). After filtration, a soln. containing 1-bromo-2-chlorocyclopropene [7] was added at –20°. The temp. was raised to 25°. The mixture was washed with H_2O (10 ml) and dried. After recrystallization (EtOH), pure **4a** was obtained (109 mg, 30%). M.p. 78–79°. IR ($CHCl_3$): 3085*w*, 3040*w*, 3005*m*, 1460*m*, 1415*m*, 1350*w*, 1288*m*, 1260*m*, 1220*m*, 1155*s*, 970*s*, 910*s*, 860*m*, 835*s*, 650v*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.4 (*m*, 2 H); 7.25 (*m*, 2 H); 5.22 (*s*, 1 H); 5.17 (*s*, 1 H); 2.32 (*AB*, $^2J_{AB}$ = 7.3, δ_A = 2.78, δ_B = 1.82, 2 H). MS: 274, 272, 270 (M^+), 245 (20), 243 (67), 241 (70), 237 (31), 235 (31), 193 (2), 191 (9), 164 (38), 163 (51), 162 (100), 149 (11), 128 (80), 127 (64), 101 (11), 77 (20), 51 (18). Anal. calc for $C_{11}H_8BrClO$: C 48,66, H 2.97; found: C 48.43, H 2.88.

*1*H-*Cyclopropa[*b*]naphthalene* (**3c**). To $TiCl_3$ (132 mg, 0.86 mmol) in THF (5 ml) under N_2 at –30°, MeLi in Et_2O (1.6 ml, 1.6M) and Et_3N (0.17 g, 1.7 mmol) were added. The cooling bath was removed, and the mixture was stirred for 0.5 h, then **4a** (50 mg, 0.18 mmol) in THF (5 ml) was added, and stirring was continued for 4 h. After workup as for **3a** and purification by prep. TLC, **3c** (15 mg) was obtained in 60% yield. The spectroscopic data are identical to those in [13].

Aromatization of **4a** *with* $TiCl_3/LiAlH_4$. The procedure was identical to that used for the synthesis of **3a**. The reaction was quenched after 2 h. The crude product contained **3c**, **5a**, **5b**, and **5c**. Compound **3c** was converted to 2-(hydroxymethyl)naphthalene by reaction with aq. $AgNO_3$ [30] and separated by prep. TLC. The remaining compounds were separated by prep. GC (10% *Carbowax*, 180°) and identified by comparison of the anal. data with those reported in [31] (**5b**) and [32] (**5c**).

Data of **5b**. M.p. 123° ([31]: 123°). ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.84 (*s*, 1 H); 7.78–7.66 (*m*, 3 H); 7.46–7.40 (*m*, 2 H); 2.52 (*s*, 3 H). MS: 178, 176 (*4:6*, M^+), 149 (46), 141 (10), 113 (16), 112 (11), 111 (16), 97 (24), 85 (29), 71 (61), 69 (49), 57 (100), 55 (63).

Data of **5c**. M.p. 127°. ^{1}H-NMR ($CDCl_3$, 200 MHz) [32]: 8.05 (*s*, 1 H); 7.78–7.66 (*m*, 3 H); 7.50–7.38 (*m*, 2 H): 2.55 (*s*, 3 H). MS: 222, 220 (M^+), 141 (100), 139 (40), 115 (31), 91 (18), 71 (21), 63 (12).

Synthesis of 2,7-Dimethyl-1*H*-cyclopropa[*g*]isoquinoline (15). – *5,8-Epoxy-5,8-dihydro-5,8-dimethylisoquinoline* (**10a**). *3-(3,3-Dimethyltriazin-1-yl)pyridinecarboxylic acid* (**7**) [21] (2.0 g, 10.4 mmol) was heated with CF_3COOH (0.8 ml, 1 equiv.), 2,5-dimethylfuran (5.5 ml, 5 equiv.), and CH_3CN (20 ml) in a sealed tube to 120° for 0.5 h. After cooling, the mixture was poured into sat. Na_2CO_3 (50 ml) and extracted with Et_2O (2 × 50

ml). The aq. layer was further extracted continuously with CH_2Cl_2 overnight. The combined org. layers were dried (Na_2SO_4) and afforded **15** (720 mg, 40%). M.p. 81–82°. IR ($CHCl_3$): 3015*s*, 2980*s*, 2920*m*, 1600*m*, 1580*w*, 1455*m*, 1420*m*, 1385*s*, 1300*m*, 1240*m*, 1230*s*, 1005*m*, 855*s*, 830*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.3 (*m*, 2 H); 7.095 (*m*, 1 H); 6.76 (*AB*, ^3J = 5.4, δ_A = 6.80, δ_B = 6.72, 2 H); 1.95 (*s*, 3 H); 1.88 (*s*, 3 H). MS: 173 (16, M^+), 172 (5), 158 (9), 147 (27), 132 (21), 131 (100), 130 (88), 115 (8), 103 (17), 91 (4), 77 (32), 63 (14), 51 (41).

When *3,4-didehydropyridine* (**8**) was generated from *3-bromopyridine* (**6**) with Li-tetramethylpiperidide [20], **10a** was obtained in 20% yield.

5,8-Epoxy-5,8-dihydroisoquinoline (**10b**). The triazene **7** (1.0 g, 5.2 mmol) was heated with CF_3COOH (0.4 ml, 1 equiv.), furan (1.80 g, 5 equiv.), and CH_3CN (10 ml) in a sealed tube to 120° for 0.5 h. After cooling, the mixture was poured in sat. Na_2CO_3 (50 ml) and extracted with Et_2O (2 × 50 ml). The aq. layer was extracted continuously with CH_2Cl_2 overnight. The combined org. layers were dried and evaporated. Yield of **10b**: 300 mg (40%). M.p. 50°. IR ($CHCl_3$): 3040*w*, 1620*w*, 1590*m*, 1415*m*, 1280*s*, 1120*m*, 1020*m*, 1000*m*, 980*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.44 (*s*, 1 H); 8.28 (*d*, ^3J = 4.4, 1 H); 7.22 (*d*, ^3J = 4.4, 1 H); 7.04 (*dd*, ^3J = 5.6, 1.8, 1 H); 6.97 (*dd*, ^3J = 5.6, 1.8, I H); 5.81 (*m*, 1 H); 5.72 (*m*, 1 H). MS: 145 (16, M^+), 129 (16), 119 (27), 117 (100), 115 (26), 105 (19), 90 (46), 89 (58), 86 (42), 84 (69), 75 (18), 63 (30).

5,8-Epoxy-5,6,7,8-tetrahydro-5,8-dimethylisoquinoline (**11a**). Compound **10a** was hydrogenated in EtOH (10 ml) in presence of 10 mg of 10% Pd on charcoal until uptake of 1 equiv. of H_2. The soln. was filtered through *Celite*, and the solvent evaporated. Isolation of **11a** in 95% yield. M.p. 68°. IR ($CHCl_3$): 3010*m*, 2980*s*, 2950*m*, 2870*w*, 1610*m*, 1440*m*, 1390*s*, 1350*m*, 1220*m*, 1100*s*, 1030*m*, 930*m*, 840*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.48 (*d*, ^3J = 4.76, 1 H); 8.4 (*d*, ^5J = 0.95, 1 H); 7.09 (*dd*, ^3J = 4.76, ^5J = 0.95, 1 H); 1.96 (*m*, 2 H); 1.86 (*s*, 3 H); 1.80 (*s*, 3 H); 1.52 (*m*, 2 H). MS: 175 (0.6, M^+), 160 (6), 148 (20), 147 (100), 146 (54), 132 (47), 117 (17), 104 (13), 77 (17), 63 (9), 51 (29).

5,8-Epoxy-5,6,7,8-tetrahydroisoquinoline (**11b**). In presence of 10 mg of Pd-catalyst (10% on charcoal), **10b**: (250 mg, 1.7 mmol) was hydrogenated in EtOH (10 ml) until uptake of 1 equiv. of H_2. The soln. was filtered through *Celite*, and the solvent was evaporated. Yield of **11b**: 240 mg (95%). M.p. 52°. IR ($CHCl_3$): 3015*s*, 2990*s*, 2960*s*, 2880*m*, 1620*m*, 1570*s*, 1470*m*, 1410*s*, 1320*s*, 1280*m*, 1230*m*, 1170*m*, 1115*w*, 1040*w*, 1020*s*, 980*s*, 940*s*, 885*m*, 855*s*, 830*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.48 (*s*, 1 H); 8.42 (*d*, ^3J = 4.6, 1 H); 7.20 (*d*, ^3J = 4.6, 1 H); 5.48 (*m*, 1 H); 5.42 (*m*, 1H); 2.20–2.00 (*m*, 2 H); 1.50–1.30 (*m*, 2 H). MS: 147 (6, M^+), 119 (100), 91 (17), 64 (8), 63 (9), 51 (9).

1a(7a)-endo-*Bromo-7a(1a)*-endo-*chloro-2,7-epoxy-1a,2,7,7a-tetrahydro-2,7-dimethyl-1*H-*cyclopropa[g]isoquinoline* (**13a**). After slow sublimation of **11a** (40 mg, 0.23 mmol) at 80°/0.1 Torr through a quartz tube (10 cm, ∅ 10 mm) and heating to 600, the pyrolysate was collected in a trap cooled to –78°. *5,7-Dimethylfuro[3,4-c]pyridine* (**12a**) was characterized by ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.82 (*s*, 1 H); 7.62 (*d*, ^3J = 6.66, 1 H); 6.94 (*dd*, ^3J = 6.66, ^5J = 1.1, 1 H); 2.65 (*s*, 3 H); 2.54 (*s*, 3 H). In parallel, 1-bromo-2-chlorocyclopropene was prepared by reaction of 1-bromo-2,2-dichloro-2-(trimethylsilyl)cyclopropane (120 mg, 0.46 mmol) with Bu_4NF (0.5 ml 1M in THF) in THF (5 ml) at –20° and cooled to –78°. The pyrolysate was diluted with THF (5 ml) and added to the cyclopropene. The temp. was allowed to rise to 10°, and H_2O (10 ml) was added. The mixture was extracted with Et_2O (2 × 20 ml), and the combined org. layers were washed with sat. NaCl (20 ml) and dried (K_2CO_3). The solvent was evaporated and the residue purified by rapid CC (SiO_2, Et_2O). Yield of **13a**: 31 mg (90% calc. with respect to sublimed **11a**). M.p. 42°. IR ($CHCl_3$): 3010*m*, 2990*m*, 2860*m*, 1610*m*, 1570*s*, 1420*m*, 1380*s*, 1325*m*, 1270*s*, 1150*s*, 1050*s*, 880*m*. ^{1}H-NMR (CD_2Cl_2, 200 MHz): 8.50 (*m*, 2 H); 7.25 (*m*, 1 H); 2.70 (*d*, ^2J = 7.3, 1 H); 1.77 (2 *s*, 3 H); 1.73 (2 *s*, 3 H); 1.65 (2 *d*, ^2J = 7.3, 1 H). MS: 224, 222, 220 (18:26:20, M^+), 180 (30), 178 (100), 177 (34), 142 (26), 115 (21), 77 (10), 63 (20), 51 (20).

1a,7a-endo-*Dibromo-2,7-epoxy-1a,2,7,7a-tetrahydro-2,7-dimethyl-1*H-*cyclopropa[g]isoquinoline* (**13b**). 1,2-Dibromocyclopropene, prepared from 1,1,2-tribromo-1-(trimethylsilyl)cyclopropane [6], was added to **12b** as described for **13a**. The adduct **13c** was isolated after rapid CC (SiO_2, Et_2O/hexane 2:1) in 82% yield (calc. on pyrolyzed **11a**). M.p. 72-73°. IR ($CHCl_3$): 2990*m*, 2960*w*, 2895*w*, 1610*m*, 1440*w*, 1420*m*, 1385*s*, 1320*m*, 1255*s*, 1220*s*, 1170*m*, 1125*w*, 980*w*, 880*m*, 850*m*, 820*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.54 (*d*, ^3J = 4.7, 1 H); 8.50 (*s*, 1 H); 7.22 (*dd*, ^3J = 4.7, ^5J = 1.3, 1 H); 2.74 (*d*, ^3J = 7.3, 1 H); 1.82, (*s*, 3 H); 1.77 (*s*, 3 H); 1.64 (*d*, ^3J = 7.4, 1 H). MS: 346/344/342 (1:2:1, M^+), 302 (14), 266 (62), 244 (64), 224 (98), 222 (100), 184 (30), 142 (36), 115 (22), 102 (50), 98 (42), 63 (18).

1a(7a)-endo-*Bromo-7a(1a)*-endo-*chloro-2,7-epoxy-1a,2,7,7a-tetrahydro-1*H-*cyclopropa[g]isoquinoline* (**13c**). Compound **11b** (40 mg, 0.27 mmol) was sublimed at 60°/0.1 Torr into a pyrolysis tube heated to 600°, and the pyrolysate **12b** was collected in a trap cooled to –78°. ^{1}H-NMR of **12b** ($CDCl_3$, 200 MHz): 9.06 (*s*, 1 H); 8.25 (*m*, 1 H); 8.04 (*m*, 1 H); 7.83 (*d*, ^3J = 6.4, 1 H); 7.20 (*m*, 1 H). 1-Bromo-2-chlorocyclopropene was prepared as described in [6] from 1-bromo-2,2-dichloro-1-(trimethylsilyl)cyclopropane (120 mg, 0.46 mmol) and allowed to react at –78° with **12b**, diluted in THF (5 ml). The temp. was allowed to reach 10°, and H_2O (10 ml) was

added. The mixture was extracted with Et_2O (2 × 20 ml), the org. layers were washed with sat. NaCl (20 ml) and dried (K_2CO_3). After evaporation of the solvent and rapid CC, 39 mg of **13a** (90%, calc. on sublimed **11b**) was isolated. M.p. 110°. IR ($CHCl_3$): 2950*s*, 2930*s*, 2850*m*, 1610*w*, 1560*w*, 1460*w*, 1420*w*, 1155*w*, 980*m*, 915*m*, 825*m*, 815*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.61 (*s*, 1 H); 8.50 (*d*, ^3J = 4.6, 1 H); 7.33 (*m*, 1 H); 5.27, 5.29, 5.20, 5.16 (4 *s*, 2 H); 2.71 (*d*, ^3J = 7.3, 1 H); 1.75 (2 *d*, ^3J = 7.3, 1 H). ^{13}C-NMR ($CDCl_3$, 200 MHz): 153.2 (C); 152.7 (C); 148.9 (CH); 148.8 (CH); 142.8 (CH); 142.7 (CH); 139.8 (C); 139.3 (C); 117.9 (CH); 81.9 (CH); 81.0 (CH); 80.6 (CH); 79.7 (CH); 51.25 (C); 50.5 (C); 41.9 (C); 40.9 (C); 30.6 (CH_2). MS: 275, 273, 271 (M^+), 246 (9), 244 (40), 242 (30), 192 (15), 166 (28), 165 (37), 164 (86), 163 (100), 129 (41), 128 (55), 102 (45), 101 (50), 76 (23), 75 (67), 74 (63), 63 (40), 51 (69), 50 (69). Anal. calc. for $C_{10}H_7BrClNO$: C 44,07, H 2.59, N 5.14; found: C 44.20, H 2.78, N 4.95.

1a(7a)-endo-*Bromo-7a(1a)-endo-chloro-2,7-epoxy-1a,2,7,7a-tetrahydro-2,7-bis(trimethylsilyl)-1*H-*cyclopropa[g]isoquinoline* (**13d**). *Furo[3,4-c]pyridine* (**12b**) was prepared from **11b** (280 mg), dissolved in THF (5 ml), and reacted at –30° with Li-tetramethylpiperidide (2.1 equiv.). The soln. turned dark immediately. After 10 min TMSCl (0.426 g, 2.1 equiv.) was added, stirring was continued at –30° for 10 min, and 200 mg of solid Na_2CO_3 were added. 1-Bromo-2-chlorocyclopropene was prepared from 1-bromo-2,2-dichloro-1-(trimethylsilyl)cyclopropane [6] (550 mg, 2.1 mmol) and purified by bulb-to-bulb distillation at –20°/0.1 Torr. Compound **12b** was added. The temp. was allowed to reach 25° overnight, and the mixture was worked up as usual. The ^{1}H-NMR of the crude product showed the expected signals of **13d**; however, purification could not be effected neither by chromatography (normal and reversed phase) nor by sublimation.

*2,7-Dimethyl-1*H-*cyclopropa[g]isoquinoline* (**15**). $TiCl_3$ (369 mg, 2.4 mmol) was mixed with BuLi (3.2 ml, 1.5M in hexane, 2 equiv.) at –70° in THF (20 ml). The cooling bath was removed, Et_3N (0.66 ml, 2 equiv.) was added, and the mixture was stirred at r.t. for 1 h. A soln. of **13a** (120 mg, 0.4 mmol) in THF (10 ml) was added, and the soln. was stirred under N_2 for 48 h, after which it was poured into 100 ml of Et_2O/sat. Na_2CO_3 1:1. The layers were separated, and the aq. phase was extracted with Et_2O (50 ml). After drying of the combined org. layers (K_2CO_3), the solvents were evaporated, and the residue was purified by rapid CC (SiO_2, Et_2O): 30 mg of **13a** and 20 mg of **14** /**15**.

Compound **15** was separated by recrystallization with pentane (10 mg, 15%). M.p. 86–88°. UV (hexane): 228 (4.198) 279 (3.284), 323 (3.125). IR ($CHCl_3$): 2958*s*, 2930*s*, 2858*m*, 1745*m*, 1640*m*, 1600*m*, 1375*m*, 1280*s*, 1180*s*, 1020*s*, 830*s*, 810*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 9.36 (*s*, 1 H); 8.54 (*d*, ^3J = 6, 1 H); 7.75 (*d*, ^3J = 6, 1 H); 3.35 (*s*, 2 H); 2.73 (*s*, 3 H); 2.61 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 148.7 (CH); 142.8 (CH); 140.4 (C); 131.5 (C); 125.1 (C); 121.9 (C); 118.6 (C); 117.8 (CH); 116.93 (C); 18.2 (CH_2); 15.4 (CH_3); 15.3 (CH_3). MS: calc. for $C_{12}H_{11}N$: 169.0891, found: 169.0889; 169 (100, M^+), 168 (54), 167 (6), 154 (69), 141 (20), 139 (12), 127 (16), 115 (20), 84 (10), 63 (16), 51 (15).

Data of **14** (position of Cl not determined). M.p. 138°. IR ($CHCl_3$): 3015*m*, 2980*m*, 2900*m*, 1600*s*, 1560*w*, 1460*w*, 1280*w*, 1205*w*, 1090*w*, 1000*m*, 920*w*, 810*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 9.47 (*s*, 1 H); 8.53 (*d*, ^3J = 6, 1 H); 7.75 (*d*, ^3J = 6, 1 H); 2.74 (*s*, 3 H); 2.72 (*s*, 3 H); 2.58 (*s*, 3 H). MS: 207, 205 (20, 100, M^+), 190 (32), 170 (60), 154 (18), 128 (10), 115 (14), 91 (17), 63 (17).

Aromatization of Cyclopropene Adducts to Furans. – *Addition of 1-Bromo-2-chlorocyclopropene to 2,5-Dimethylfuran* (**9a**). *1a*-endo-*Bromo-5a*-endo-*chloro-2,5-epoxy-1a,2,5,5a-tetrahydro-2,5-dimethyl-1*H-*cyclopropabenzene* (**17a**). The procedure was that described in detail for **17b**. Yield of **17a**: 60%. IR ($CHCl_3$): 3005*m*, 2990*m*, 2940*m*, 1450*s*, 1415*m*, 1385v*s*, 1315*s*, 1270*m*, 1175*m*, 1150*s*, 1055v*s*, 1040*m*, 988*m*, 935*m*, 913*w*, 900*m*, 865*s*, 845*w*, 705 v*s*. ^{1}H-NMR (CD_2Cl_2, 200 MHz): 6.48 (*s*, 2 H); 2.08 (*AB* , $^2J_{AB}$ = 7, δ_A = 2.58, δ_B = 1.51); 1.53 (*s*, 6 H). MS: 252, 250, 248 (M^+), 237 (5), 235 (11), 233 (10), 223 (26), 221 (32), 209 (14), 207 (50), 205 (43), 169 (46), 134 (23), 128 (32), 126 (100), 105 (18), 96 (41), 91 (88), 77 (18), 65 (38), 51 (38).

Addition of 1-Bromo-2-chlorocyclopropene to 2-Methylfuran. 1a-endo-*Bromo-5a*-endo-*chloro-2,5-epoxy-1a,2,5,5a-tetrahydro-2(5)-methyl-1*H-*cyclopropabenzene* (**17b**). 1-Bromo-2-chlorocyclopropene was prepared as usual [6] from 1-bromo-2,2-dichloro-1-(trimethylsilyl)cyclopropane (2.0 g, 7.6 mmol) in presence of 2-methylfuran (15 ml) at 40°. The temp. was raised to –20° and maintained for 2 h, then it was allowed to reach 25°. After addition of Et_2O (25 ml), the mixture was extracted with H_2O (2 × 20 ml) and sat. NaCl (30 ml), the org. layer dried ($MgSO_4$) and evaporated under reduced pressure. The product was purified by sublimation with a bulb-tube: 1.0 g (56%) of **7b**. M.p. 45–48°. IR ($CHCl_3$): 3005*m*, 2980*m*, 2935*w*, 1448*m*, 1412*m*, 1385*s*, 1315*s*, 1285*m*, 1170*s*, 985v*s*, 940*s*, 915*m*, 885*m*, 875*m*, 855*m*, 830*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 6.69 (*m*, 1 H); 6.52 (*m*, 1 H); 4.82 (*m*, 1 H); 2.10 (*AB* , $^2J_{AB}$ = 7.6, δ_A = 2.65, δ_B = 1.60); 1.62 (3 H). MS: 236 (3, M^+), 223, 221, 219 (3:9:7), 201 (6), 199 (6), 193 (19), 191 (15), 155 (12), 126 (18), 119 (48), 91 (60), 86 (63), 84 (100), 83 (56), 77 (17), 65 (20), 51 (24), 47 (36).

Addition of 1-Bromo-2-chlorocyclopropene to Furan. 1a-endo-*Bromo-5a*-endo-*chloro-2,5-epoxy-1a,2,5,5a-tetrahydro-1*H-*cyclopropabenzene* (**17c**) *and its* exo-*Isomer*. The same procedure using furan afforded a mixture of *exo* and *endo* adducts in 48% yield, separable by prep. TLC (hexane/AcOEt 20:1).

Data of **17c** (*exo* CH_2). ^{1}H-NMR: 6.73 (*s*, 2 H); 4.91 (*s*, 1 H); 4.84 (*s*, 1 H); 2.70 (*d*, ^3J = 7, 1 H); 1.70 (*d*, ^3J = 7, 1H).

Data of **17c** (*endo* CH_2). ^{1}H-NMR: 6.41 (*m*, 2 H); 5.15 (*m*, 1 H); 5.05 (*m*, 1 H); 2.24 (*d*, ^3J = 7.5, 1 H); 1.96 (*d*, ^3J = 7.5, 1 H).

Reaction of Adducts **17a–c** *with* $TiCl_3/LiAlH_4$. *1-Bromo-6-chloro-2,5-dimethylcyclohepta-1,3,5-triene* (**18a**). The procedure is described in detail for **18b**. Yield 30% of **18a**, but no trace **19b**. IR ($CHCl_3$): 3005*m*, 2960*m*, 2925*m*, 2880*w*, 2860*w*, 1630*w*, 1615*m*, 1525*m*, 1415*m*, 1378*m*, 1305*m*, 1260*w*, 1250*w*, 1235*m*, 1215*w*, 1200*m*, 1110*w*, 1080*s*, 795*m*, 770*s*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 6.33 (*s*, 2 H); 3.22 (*s*, 2 H); 1.98 (*s*, 3 H); 1.95 (*s*, 3 H). MS: 236, 234,232 (4:14:11, M^+), 199 (20), 197 (20), 155 (32), 153 (100), 117 (24), 115 (38), 103 (11), 91 (32), 63 (16), 51 (14).

*2-Methyl-1*H-*cyclopropabenzene* (**19a**) *and 1-Bromo-6-chloro-2(5)-methylcyclohepta-1,3,5-triene* (**18b**). $TiCl_3$ (3.01 g, 19.5 mmol) was reacted with $LiAlH_4$ (0.38 g, 10 mmol) in THF (50 ml), **17b** was added (1.0 g, 4.2 mmol), and the mixture was stirred for 20 h. It was hydrolyzed with sat. Na_2CO_3 (20 ml), then extracted with pentane (2 × 50 ml). After drying (K_2CO_3), the solvent was evaporated at 0° under reduced pressure. The resulting oil (650 mg) contained **18b** (30%), **19a** (30%), and THF, according to GC (*SE 30*, 40°). A sample of **19a** was separated by prep. GC and showed identical spectral data as reported by *Garratt* and coworkers [25]. ^{1}H-NMR ($CDCl_3$, 200 MHz): 6.9–7.1 (*m*, 3 H); 3.08 (*s*, 2 H); 2.33 (*s*, 3 H). MS: 105 (100, $[M + 1]^+$), 104 (30, M^+), 103 (18), 91 (18), 84 (14), 79 (27), 77 (27), 63 (7), 49 (22).

2-Bromo-6-chlorocyclohepta-1,3,5-triene (**18c**) *from Thiophene Dioxide* (**21**). Compound **21** was prepared in THF from dibromosulfolane (8 mmol) according to *Lemal et al.* [28]. In parallel, 1-bromo-2-chlorocyclopropene was synthesized from 1-bromo-2,2-dichloro-1-(trimethylsilyl)cyclopropane (6.4 mmol, 0.8 equiv.) in THF (5 ml) at –20°. To this was added the thiophene dioxide soln. *via* filtration through a 4-cm column of *Celite* under N_2. After 16 h at –20°, the mixture was poured in Et_2O (100 ml) and H_2O (100 ml). The aq. phase was extracted with Et_2O (100 ml), and the combined org. layers were dried ($MgSO_4$) and evaporated. After addition of pentane (50 ml), the soln. was filtered in order to remove polymeric material. The product was then purified by flash chromatography (SiO_2/hexane) to yield **18c** (66 mg, 5%). IR ($CHCl_3$): 3050*s*, 2990*w*, 1620*w*, 1610*w*, 1435*w*, 1420*m*, 1250*m*, 1045*w*, 955*m*, 890*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 6.57–6.25 (*m*, 4 H); 3.22 (*s*, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): 129.35 (CH); 129.30 (CH); 128.7 (CH); 125.1 (CH); 120.8 (C); 108.7 (C); 47.52 (CH_2). MS: 208/ 206/204 (7:20:16, M^+), 207 (4), 205 (6), 203 (5), 171 (29), 169 (29), 127 (33), 125 (100), 90 (18), 89 (36), 63 (24), 55 (24).

*1*H-*Cyclopropabenzene* (**19b**) *from* **18c** *and BuLi*. Compound **18c** (30 mg, 0.156 mmol) in THF (2 ml) was reacted at –78° with 200 µl of BuLi (1.6M) in hexane. Undecane (30 µl, 0.145 mmol) was added as internal standard, and the temp. was allowed to reach –30° in 2 h. The soln. was decomposed by adding 5 ml of 10% aq. $AgNO_3$. It was extracted with CH_2Cl_2 (3 × 5 ml), dried ($MgSO_4$), and evaporated. The residue was analyzed by GC (5% *SE 30*, 100°), showing the presence of benzyl alcohol in 50% yield. An anal. sample was obtained by prep. GC and identified by NMR.

Reaction of **18c** *with* $TiCl_3/LiAlH_4$. $TiCl_3$ (75 mg, 0.5 mmol) in THF (2.0 ml) was reacted with $LiAlH_4$ (2.5 mmol) for 1 h. Compound **18c** was added (20 mg, 0.097 mmol) in THF (1.0 ml) and 20 µl of undecane as internal standard. After stirring for 24 h, the soln. was decomposed and analyzed as above. Yield: 11% of benzyl alcohol.

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