Preparation and Rearrangement of Arylhydroxymethano[3]orthocyclo-[5](1,8)naphthalenophanes.

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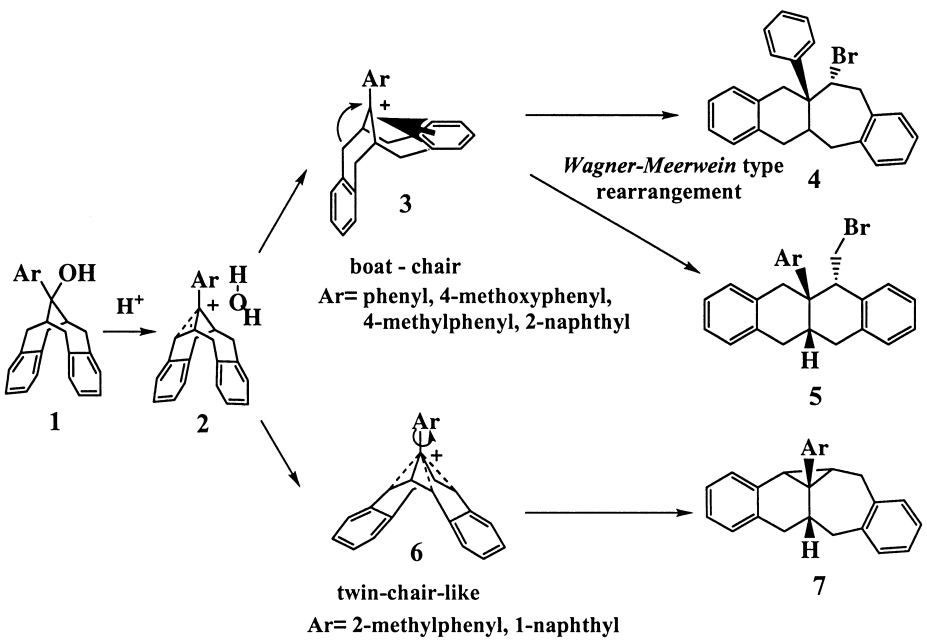
Arylhydroxymethano[3]orthocyclo[5](1,8)naphthalenophanes **11**, which possess a rigid boat-chair conformation, were prepared by the reaction of 9,10-benzo-3,4,5-[1,8]naphthobicyclo[5.4.1]dodecan-3,9-dien-12-one **8c** with aryllithium reagents and treated with hydrobromic acid in dioxane. The intermediary cation generated from **11** rearranged either to a benzo[*cd*]azulene system of type **12** or to a tricyclic system containing a cyclopropane-unit of type **13**, depending on the nature of the aryl substituent on the bridging carbon atom.

Recently, it was reported that the behavior of the tertiary benzylic cation, generated from the 11-aryl-3,4:8,9-dibenzobicyclo[4.4.1]undeca-3,8-dien-11ol **1** by a treatment with hydrobromic acid in dioxane, is dependent upon the nature of the aryl-substituent on the methano bridge of the bicyclo[4.4.1]undecane skeleton.[1] Benzylic cations of type **3** with a neighboring phenyl or with a neighboring electron-rich aryl group, such as the *p*-methylphenyl, *p*-methoxyphenyl, and 2-naphthyl group, are thought to take a chair-boat conformation[2] and undergo a *Wagner–Meerwein* rearrangement to a secondary cation. The bromide ion in solution reacts with the cation to form the final product **4** with a fused 6–7 ring system (Scheme 1). The secondary cation formed can also undergo a second, phenonium ion-driven rearrangement that leads to an intermediate species with a spiro[2.5]octadienyl cation subunit. The bromide then reacts with the spirocyclopropane of that subunit to give compound **5** with a fused 6–6 ring system. When the aryl group is bulky, as in the case of a 2-methylphenyl or 1-naph-



Scheme 1.

Fig. 1. 9,10-Benzo-3,4,5-[1,8]naphthobicyclo[5.4.1]dodeca-3,9-diene systems **8a** and **8c**.

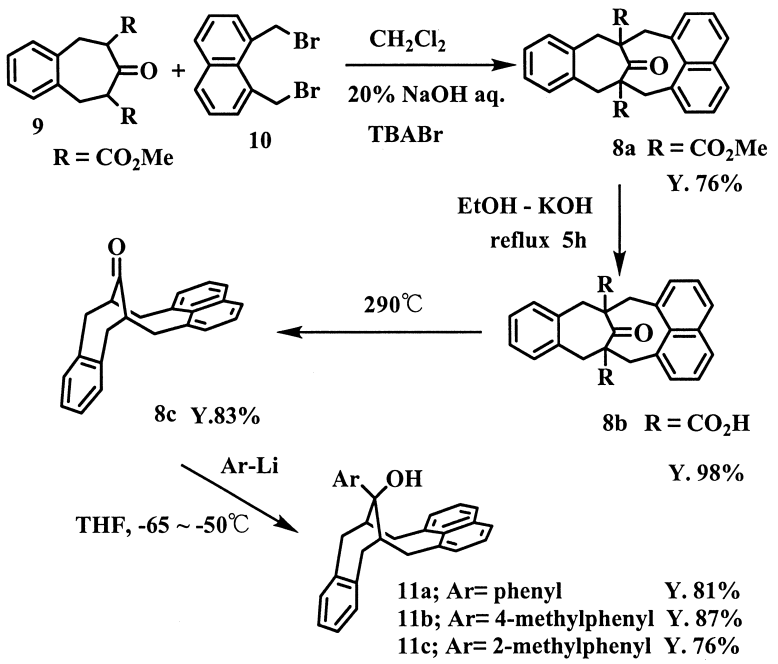
thyl group, the benzylic cation takes a twin-chair-like conformation. This leads to added strain in the benzylic position and the reaction proceeds via a non-classical cation of type **6** (Scheme 1), furnishing **7**, compounds with a cyclopropane unit (Scheme 1). It is supposed that in all of the primarily formed carbocations **2** there is a stabilization of the bridge-cation by the strained benzylic methylene carbons opposite to the leaving group. The interaction with the methylene carbons increases with the departure of the leaving group. Therefore, the rotational barrier for the aryl substituent is lower than that in a non-stabilized benzyl cation.[3,4] Depending on the steric demand of the rotating aryl substituent the cation will either take a boat-chair conformation (for a less bulky aryl group) or a twin-chair conformation (for bulky substituents). The boat-chair conformed structure may involve a cation-π interaction of the benzylic cation with the benzo-unit annelated to the boat-conformed cycloheptane (see **3**). This stabilization may weaken the cation interaction with the benzylic carbons of the chair-conformed cycloheptene at this stage. The cation then passes through the rearrangements explained above. In the case of the cations taking a twin-chair conformation (bulky aryl substituents), no cation-pi interaction of the benzyl cation with any one of the annelated benzo units is possible, and thus the authors have proposed a stabilization of the cation involving all four benzylic carbons, as shown in Scheme 1.

9,10-Benzo-3,4,5-[1,8]naphthobicyclo[5.4.1]dodecadiene systems **8a** and **8b** with an sp^2-hybridized carbon in the bridge, which are precursors of alcohols **11**, and ultimately of the cations generated from **11**, adopt a rigid boat-chair conformation, in which the eight-membered ring takes the boat form (Fig. 1).[5]

The intermediately formed benzylic cation generated from 12-aryl-9,10-benzo-3,4,5-[1,8]naphthobicyclo[5.4.1]dodeca-3,9-dien-12-ol **11** may reasonably be supposed to be fixed in the boat-chair conformation, too. Because a rigid boat-chair conformation could not be realized with cations generated from **1**, the reactivity of the cations generated from **11** was expected to be different from that of the cations of **1**. A description of this reactivity is the aim of the present paper, which presents the preparation and acid-catalyzed transformation of **11**.

Results and Discussion

Preparation of Alcohol 11. 9,10-Benzo-3,4,5-[1,8]naphthobicyclo[5.4.1]dodeca-3,9-dien-12-one **8c** was prepared in a three-step procedure. 1,8-Bis(bromomethyl)naphthalene **10** was reacted with dimethyl 7-oxa-6,7,8,9-tetrahydrobenzo-5*H*-cycloheptene-6,8-dicarboxylate **9** under phase-transfer conditions in the presence of a strong base to give dimethyl 12-oxo-9,10-benzo-3,4,5-[1,8]naphtho-bicyclo[5.4.1]dodeca-3,9-diene-1,7-dicarboxylate **8a** in 94% yield. An alternative route using dimethyl 9-oxo-8,9,10,11-tetrahydro[1,8]naphtho-7*H*-cyclooctene-8,10-dicarboxylate and 1,2-bis(bromomethyl)-benzene gave **8a** in a more moderate yield (49%), as had been reported previously.[6] The subsequent hydrolysis of **8a** and decarboxylation of the corresponding dicarboxylic acid **8b** gave ketone **8c** in 83% yield. Ketone **8c** is fixed in a boat-chair conformation[3] and is unreactive towards arylmagnesium halides (Grignard reagents). However, the desired alcohols **11a–c** could be obtained by reacting **8c** with aryllithium reagents (Scheme 2).[7a–7c] The aryl anions react with the carbonyl group



Scheme 2.

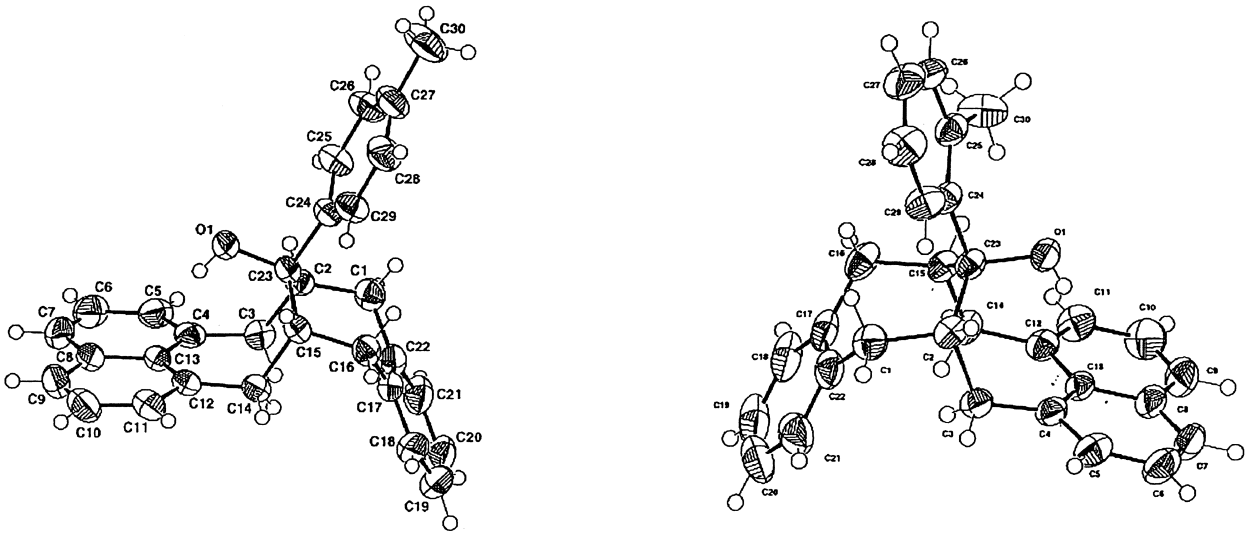
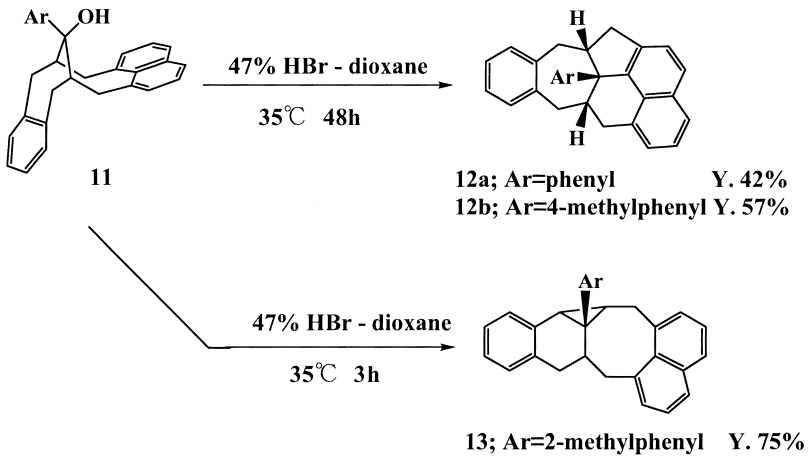


Fig. 2. ORTEP Drawings **11b** and **11c**.



Scheme 3.

of **8c** from the less congested side of the seven-membered ring and the hydroxy group in **11a–c** comes to rest above the 1,8-naphtho-annelated eight-membered ring. The structures of the alcohols **11a–c** were established by means of ^{13}C NMR spectroscopy and X-ray crystallographic analyses of **11b** and **11c** (Fig. 2).

Treatment of 11 with HBr. 12-Aryl-9,10-benzo-3,4,5-[1,8]naphthobicyclo[5.4.1]dodeca-3,9-dien-12-ols **11** were treated with 47% hydrobromic acid in dioxane for 48 h at 35 °C (Scheme 3).

It was found that in this reaction the phenyl-substituted orthocyclophane alcohol **11a** and the 4-methylphenyl-substituted orthocyclophane alcohol **11b** each gave a single product, **12a** and **12b**, in 42% and 57% yield, respectively. X-Ray crystallographic analysis disclosed the structure **12a**, which has a seven-, a six-, and a five-membered ring fused to form a hexahydro-1*H*-benzo[*cd*]azulene core unit (Fig. 3).[8]

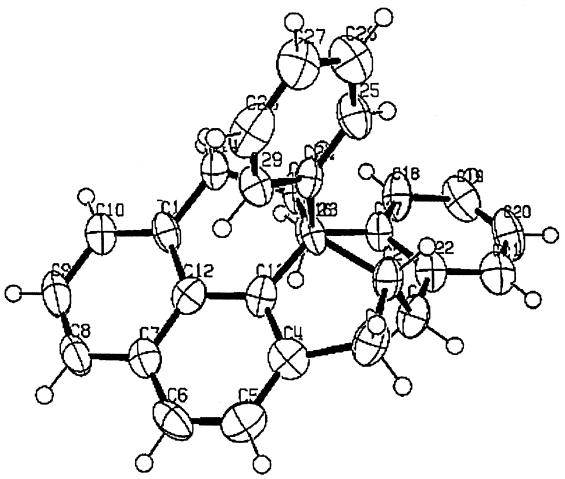


Fig. 3. ORTEP Drawing of **12a**.

The reaction of 2-methylphenyl-alcohol **11c** with hydrobromic acid was completed in a short time (3 h) and gave **13** in 75% yield (Scheme 3). This reflects the reactivity shown by the corresponding methano[3.3]orthocyclophane alcohols **1**, described above.[1] However, it must be noted that, in contrast

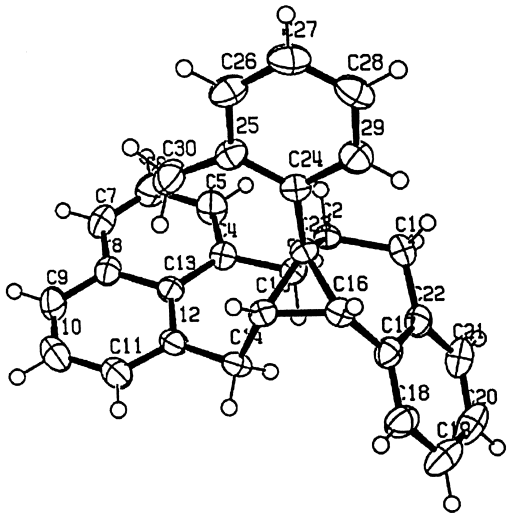


Fig. 4. ORTEP Drawing of **13**.

to **1** or the cation generated from **1**, neither **11** nor the cation generated from **11** can take a chair-chair conformation, because the benzo- and naphtho-units would be too near to each other.

The structure of **13** was determined by X-ray crystallographic analysis. In product **13**, the original benzo-1,8-naphtho-bicyclo[5.4.1]dodecadiene system of **11c** was maintained. A carbon–carbon bond has been formed between the benzylic position in the seven-membered chair conformed ring and the cationic center on the bridge, giving a cyclopropane-ring as a sub-structure of **13** (Fig. 4).

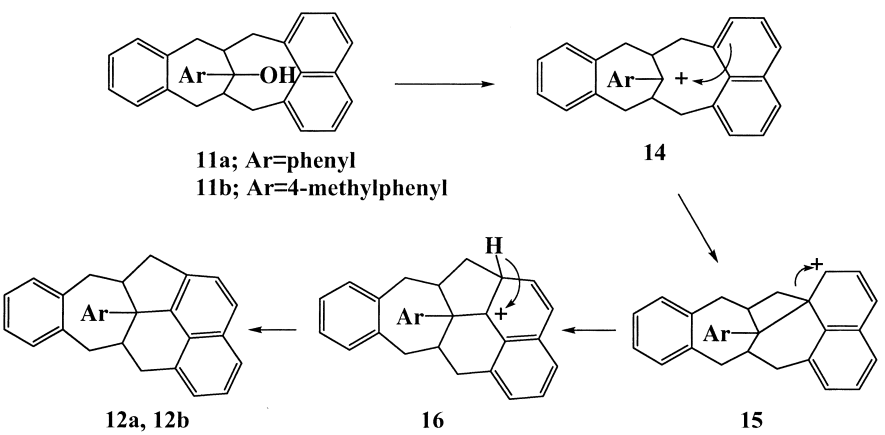
The sterically protected cyclopropane-ring[9] of **13** is stable under acidic reaction conditions; **13** could be recovered quantitatively after being treated with 47% hydrobromic acid for 24 h.

Reaction Pathway. During the course of the reaction of alcohols **11a** and **11b** with hydrobromic acid, the benzocycloheptenone substructure, which rests in a chair-conformation, does not react. Instead, the eight-membered ring substructure is transformed to an indane skeleton. In the process, two carbon-carbon bonds are formed, one between the methylene bridge and the α-position of the 1,8-naphtho group, and the other between the benzylic carbon and the β-position of the 1,8-naphtho ring, while the carbon–carbon bond between the benzylic carbon and the α-position of the 1,8-naphtho group is cleaved. The mechanism of the formation of **12a** and **12b** is proposed in Scheme 4.

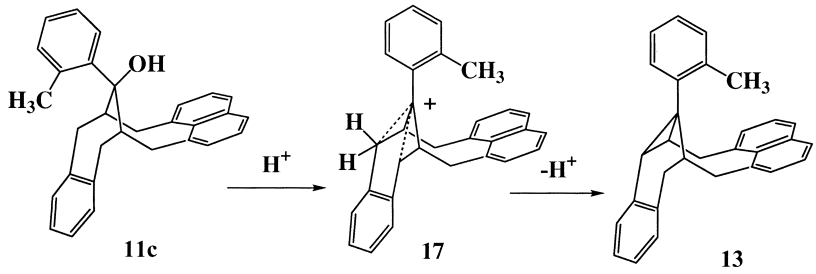
The methano[3]orthocyclo[3](1,8)naphthalenophane-cation is generated from the corresponding alcohols, **11a** and **11b**, by dehydration under acidic condition. The elimination of the hydroxy group reduces the steric congestion at the C1-bridge of the bicyclo[5.4.1]dodecadiene structure. It may well be that the formation of the cation is aided by an interaction with the strained benzylic methylene carbons opposite to the leaving group, as discussed above for the rearrangement of the cations derived from 11-aryl-3,4:8,9-dibenzobicyclo[4.4.1]undeca-3,8-dien-11-ols **1**. The cationic center in **14** comes close enough to the π-electrons of the 1,8-naphto ring to interact with the 1,8-naphtho-ring, leading to a Friedel–Crafts type alkylation and giving the cyclohexadienyl intermediate cation **15**. A *Wagner–Meerwein* rearrangement, followed by deprotonation of the rearranged cation **16**, gives the products **12a** and **12b**, respectively.

The cation generated by the treatment of alcohol **11c** with hydrobromic acid carries a bulky 2-methylphenyl group. As described above, and also for the primary cation generated from **1**, it is supposed that there is a stabilizing interaction between the benzylic methylene carbons opposite to the leaving group. Again, the rotational barrier for the aryl group will be lowered. Because the experiments were carried out at 35 °C, the 2-methylphenyl group should have undergone rotation along the bond connecting it to the cationic centre. If that is the case, then the methyl group would hinder an interaction between the cationic center and the α-position of the 1,8-naphtho ring. Rather, the primarily formed cation could form a cyclopropane containing product **13** directly from the non-classical cation **17**, as shown in Scheme 5.

It may well be that the acceleration witnessed for the rearrangement of **11c** to **13** may be due to the fact that there is a greater initial release of energy due to a greater decrease in steric crowding when going from **11c** to **17** than when proceeding from **11a/b** to **14**. Nevertheless, all of the reactions leading to the cationic species should be reversible. The formation of **13** itself, however, seems to be irreversible under the reaction conditions (see above).



Scheme 4.



Scheme 5.

Conclusion

Upon a treatment with hydrobromic acid in dioxane, 12-aryl-9,10-benzo-3,4,5-[1,8]naphthobicyclo[5.4.1]dodeca-3,9-dien-12-ols **11**, molecules which possess a rigid boat-chair conformation, undergo rearrangement reactions to different tricyclic systems. The outcome of the rearrangement of the aryl cation generated is dependent upon the nature of the aryl substituent on the bridging tertiary carbon atom, where especially the steric demand of the phenyl substituent plays an important role. Phenyl-**11a** and 4-methylphenyl-alcohol **11b** gave **12a** and **12b**, respectively. Alcohol **11c** with a bulky 2-methylphenyl group gave **13**.

Experimental

Mps were measured on a Yanako micro melting point apparatus and are uncorrected. IR spectra were measured with a JASCO IR-700. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer. The chemical shifts are relative to TMS. Mass spectra were measured with a NipponDenshi JIR-AQ2OM. Column chromatography was carried out on Wako-gel C-300 (silica gel). Recycling Preparative HPLC was done on a Japan Analytical Industry LC-908 Recycling Preparative HPLC (chloroform).

Dimethyl Naphtho[3,4,5-*de*]benzo[9,10]bicyclo[5.4.1]dodeca-3,9-dien-12-one-1,6-dicarboxylate 8a. To a stirred mixture of tetrabutylammonium bromide (0.55 g, 1.98 mmol) and 23% aq NaOH (9 mL) in dichloromethane (6 mL) was added dropwise a solution of 1,8-bis(bromomethyl)naphthalene[10] **10** (0.94 g, 3.00 mmol) and dimethyl benzo[*d*]cycloheptenone-6,8-dicarboxylate **9** (0.71 g, 3.00 mmol) in dichloromethane (6 mL) for 1 h. After the mixture was stirred for 6 h at rt, the organic phase was separated, washed with water (50 mL × 2), dried over anhydrous $MgSO_4$, and evaporated in vacuo, leaving a residue which, upon tituration with methanol, gave **8a** (9.10 g, 94%) as colorless prisms, mp 190–193 °C; lit,[6] 188–191 °C.

12-Oxo-9,10-benzo-3,4,5-[1,8]naphthobicyclo[5.4.1]dodeca-3,9-diene-1,7-dicarboxylic Acid 8b. A mixture of **8a** (1.20 g, 2.80 mmol) and powdered potassium hydroxide (3.60 g, 6.40 mmol) in ethanol (31 mL) was heated under reflux for 3 h and thereafter poured into water (80 mL). The solution was acidified with concentrated hydrochloric acid and kept at rt for 14 h. The precipitates formed were filtered to give **8b** (1.10 g, 98%) as a colorless solid, mp 290–300 °C (decomp.); IR (KBr) 3600–3200, 3024, 1731, 1434, 1219, 771 cm^{-1}; MS (FAB) *m/z* 401 ($M^+ + 1$). HRMS Found: 401.1389. Calcd. for $C_{27}H_{24}O_5$: 401.1389. Found: C, 75.68; H, 5.64%. Calcd for $C_{23}H_{20}O$: C, 75.62; H, 5.67%.

9,10-Benzo-3,4,5-[1,8]naphthobicyclo[5.4.1]dodeca-3,9-dien-12-one 8c. Dicarboxylic acid **8b** (1.10 g, 2.75 mmol) was heated in vacuo (0.2–0.4 Torr) at 320 °C until the gas evolution ceased (1 Torr ≈ 133.322 Pa). The pyrolysate was dissolved in dichloromethane (20 mL) and insoluble materials were filtered off. The filtrate was evaporated in vacuo to leave a residue, which upon column chromatography (eluent: chloroform) gave **8c** (700 mg, 78%) as a colorless solid, mp 251–253 °C; IR (KBr) 3034, 2904, 1694, 1494, 1451, 1342, 878, 775 cm^{-1}; ^{1}H NMR (270 MHz) δ 2.61–2.69 (dd, J = 5.9 and 5.3 Hz, 2H), 2.88–3.04 (m, 6H), 3.47–3.59 (t, J = 13.5 Hz, 2H), 7.13–7.30 (m, 8H), 7.58–7.62 (dd, J = 1.3 and 1.7 Hz, 2H); ^{13}C NMR (67.8 MHz) δ 37.75, 39.93, 56.39, 125.69, 127.65, 129.47, 130.22, 130.42, 131.21, 131.41, 135.92, 136.89, 138.25, 216.15; MS (EI) *m/z* 312 (M^+). HRMS Found: 312.1510. Calcd for $C_{23}H_{20}O$: 312.1514. Found: C, 88.43; H, 6.45%. Calcd for $C_{23}H_{20}O$: C, 88.40; H, 6.47%.

Preparation of Aryllithium Solution. Under an atmosphere of argon, a 50 mL three-necked flask equipped with a sealed, teflon-paddle stirrer, a thermometer, a gas inlet tube, and a dropping funnel was charged with anhydrous tetrahydrofuran (THF) (15 mL) and lithium dispersion (30 wt% in paraffin, 1.40 g, 0.60 mol). The stirred mixture was cooled to −20 °C with a dry-ice/methanol bath and a solution of aryl bromide (0.30 mol) in anhydrous THF (5 mL) was added dropwise over a period of 30 min. Thereafter, the mixture was stirred for 5–10 h at −20 °C.

12-Phenyl-9,10-benzo-3,4,5-[1,8]naphthobicyclo[5.4.1]-dodeca-3,9-dien-12-ol 11a. A solution of phenyllithium in THF (0.96 mL, 1.78 mmol), prepared according to the procedure described above, was added dropwise to a mixture of **8c** (300 mg, 0.96 mmol) in THF (16 mL) at −80 °C under argon and the mixture was kept at −70 °C for 15 h. Then, a 15 wt% aq NH_4Cl solution (10 mL) was added at −20 °C. The organic phase was separated and the aqueous layer was extracted with ether (30 mL × 2). The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated in vacuo, leaving a residue which, on recrystallization from benzene, gave **11a** (300 mg, 81%) as a colorless solid, mp 247–249 °C; IR 3546, 3056, 1493, 1181, 760 cm^{-1}; ^{1}H NMR (270 MHz, CD_2Cl_2) δ 1.56 (s, 1H), 2.90–3.03 (m, 4H), 3.17–3.22 (d, J = 14.5 Hz, 2H), 3.40–3.59 (m, 2H), 3.64–3.68 (m, 2H), 7.14–7.40 (m, 13H), 7.59–7.71 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 39.09, 40.94, 43.60, 81.46, 125.05, 125.73, 126.43, 126.63, 126.81, 128.14, 128.23, 128.32, 128.68, 129.02, 129.15, 130.87, 134.12, 134.74, 138.98, 139.21, 145.84; MS (EI) *m/z* 390 (M^+). HRMS Found: 390.1984. Calcd for $C_{29}H_{26}O$: 390.1986. Found: C, 89.11; H, 6.74%. Calcd for $C_{29}H_{26}O$: C, 89.19; H, 6.71%.

12-(*p*-Methylphenyl)-9,10-benzo-3,4,5-[1,8]naphthobicyclo-[5.4.1]dodeca-3,9-dien-12-ol 11b. A solution of *p*-methylphenyllithium in THF (1.5 mL, 2.02 mmol, prepared from *p*-bromotoluene [5.13 g, 30 mmol] and lithium dispersion [1,40 g, 0.60 mol], as described above) was added dropwise to a solution of **8c** (350 mg, 1.11 mmol) in THF (25 mL) at −60 °C under argon; the mixture was kept at −70 °C for 3 h. Then, a 15 wt% aq NH_4Cl so-

lution (10 mL) was added at −20 °C. The organic phase was separated and the aqueous layer was extracted with ether (30 mL × 2). The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated in vacuo, leaving a residue which, upon recrystallization from benzene, gave **11b** (394 mg, 87%) as a colorless solid, mp 322–325 °C; IR (KBr) 3554, 3016, 1452, 1037, 775 cm^{-1}; ^1H NMR (270 MHz, CD_2Cl_2) δ 1.48 (bs, 1H), 2.81–3.01 (m, 4H), 3.21–3.48 (m, 3H), 3.57–3.67 (m, 2H), 7.10–7.25 (m, 10H), 7.28–7.36 (m, 2H), 7.44–7.61 (m, 2H); ^{13}C NMR (67.8 MHz, CD_2Cl_2) δ 39.42, 79.19, 124.09, 125.35, 125.82, 126.07, 126.22, 127.34, 128.35, 129.76, 130.42, 132.25, 133.12, 138.97, 139.84, 143.16; MS (EI) *m/z* 404 (M^+). HRMS Found: 404.2143. Calcd for $C_{30}H_{28}O$: 404.2140. Found: C, 88.84; H, 6.99%. Calcd for $C_{30}H_{28}O$: C, 89.06; H, 6.97%.

12-(*o*-Methylphenyl)-9,10-benzo-3,4,5-[1,8]naphthobicyclo-[5.4.1]dodeca-3,9-dien-12-ol 11c. A solution of *o*-methylphenyllithium in THF (1.5 mL, 2.02 mmol, prepared from *o*-bromotoluene [5.13 g, 30 mmol] and lithium dispersion [1.40 g, 0.6 mol]) was added dropwise to a mixture of **8c** (400 mg, 1.20 mmol) in THF (21 mL) at −60 °C under argon; the mixture was kept at −60 °C for 6 h. Then, a 15 wt% aq NH_4Cl solution (10 mL) was added at −20 °C. The organic phase was separated and the aqueous layer was extracted with ether (30 mL × 2). The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated in vacuo, leaving a residue which, upon recrystallization from benzene, gave **11c** (370 mg, 76%) as a colorless solid, mp 320–325 °C; IR (KBr) 3556, 3008, 1453, 1040, 761 cm^{-1}; ^1H NMR (270 MHz, CD_2Cl_2) δ 1.55 (s, 1H), 2.77–2.99 (m, 4H), 3.25–3.31 (d, J = 14.5 Hz, 2H), 3.55–3.69 (m, 4H), 7.05–7.35 (m, 12H), 7.44–7.48 (d, J = 1.7 Hz, 2H); ^{13}C NMR (67.8 MHz, CD_2Cl_2) δ 20.83, 39.19, 41.02, 43.76, 81.27, 125.03, 125.69, 126.22, 126.41, 128.25, 128.35, 128.96, 129.34, 130.89, 134.28, 134.75, 136.37, 139.10, 139.40, 143.12; MS (EI) *m/z* 404 (M^+). HRMS Found: 404.2149. Calcd for $C_{30}H_{28}O$: 404.2140. Found: C, 88.80; H, 6.94%. Calcd for $C_{30}H_{28}O$: C, 89.06; H, 6.97%.

Rearrangement of 11a. To a solution of **11a** (150 mg, 0.38 mmol) in dioxane (14 mL) was added dropwise 47% hydrobromic acid (3.90 g, 23.1 mmol) at 35 °C and the reaction mixture was stirred at the same temperature for 48 h. Then, ether (50 mL) was added and the organic phase was separated, washed with water (50 mL) and dried over anhydrous $MgSO_4$. Thereafter, the organic phase was evaporated in vacuo to leave a residue, which was subjected to column chromatography on silica gel (Wako-gel, C-300/ eluent: toluene), giving a mixture of **12a** and an unidentified, instable product. The mixture was subjected to recycle-GLC (eluent: chloroform) for 72 h, giving **12a** (61 mg, 42%) as a colorless solid, mp 168–170 °C; IR (KBr) 2928, 1601, 1489, 1454, 1132, 774 cm^{-1}; ^1H NMR (270 MHz, CD_2Cl_2) δ 2.34 (d, J = 13.8 Hz, 1H), 2.42–2.53 (m, 2H), 2.54–2.56 (m, 1H), 2.62–2.65 (dd, J = 15.9, 2.4 Hz, 1H), 2.71–2.75 (t, J = 14.4 Hz, 1H), 2.86–2.93 (m, 2H), 3.01–3.04 (m, 1H), 6.98–7.02 (dd, J = 14.4, 7.4 Hz, 1H), 7.05–7.27 (m, 5H), 7.32–7.56 (m, 1H), 7.48–7.49 (d, J = 8.2 Hz, 1H), 7.73–7.77 (dd, J = 19.1, 8.1 Hz, 2H); ^{13}C NMR (67.8 MHz, CD_2Cl_2) δ 36.32, 37.32, 38.80, 39.97, 42.73, 53.82, 59.64, 124.04, 124.32, 125.52, 125.57, 125.91, 131.55, 132.74, 138.30, 139.47, 139.96, 143.12, 148.77; MS (EI) *m/z* 372 (M^+). HRMS Found: 372.5115. Calcd for $C_{29}H_{24}$: 372.5124. Found: C, 92.68; H, 6.41%. Calcd for $C_{29}H_{24}$: C, 93.51; H, 6.49%.

Rearrangement of 11b. To **11b** (200 mg, 0.49 mmol) in dioxane (14 mL) was added dropwise hydrobromic acid (47 wt% aq, 5.20 g, 29.7 mmol) and the resulting mixture was stirred at 35 °C for 48 h. Ether (50 mL) was added and the phases were separated. The organic phase was washed with water (50 mL) and dried over anhydrous Na_2SO_4. After concentration of the solution in vacuo, the residue was subjected column chromatography on silica gel (eluent toluene) to give a mixture of two products. Subsequently, the mixture was separated by GLC for 72 h to give **12b** (121 mg, 57%) as a colorless solid, mp 195–198 °C; IR (KBr) 2922, 1513, 1474, 1453, 1098, 777, 746 cm^{-1}; ^1H NMR (270 MHz, CD_2Cl_2) δ 2.21 (s, 3H), 2.39–2.46 (m, 2H), 2.49–2.52 (d, J = 7.25 Hz, 1H), 2.60–2.71 (m, 2H), 3.74–3.79 (m, 1H), 2.83–2.88 (d, J = 13.5 Hz, 1H), 2.94–2.98 (m, 2H), 3.07–3.13 (d, J = 15.2 Hz, 1H), 7.16–7.37 (m, 9H), 7.40–7.42 (d, J = 7.3 Hz, 1H), 7.53–7.56 (d, J = 8.2 Hz, 1H), 7.78–7.84 (m, 2H); ^{13}C NMR (67.8 MHz, CD_2Cl_2) δ 20.86, 36.30, 37.25, 38.74, 39.95, 42.70, 53.75, 59.23, 123.93, 124.24, 125.42, 125.46, 126.29, 126.52, 126.66, 127.87, 128.16, 128.61, 128.89, 131.48, 132.74, 135.31, 138.47, 139.37, 139.96, 143.12, 145.69; MS (FAB) *m/z* 386 (M^+). HRMS (FAB) Found: *m/z* 386.5385. Calcd for $C_{30}H_{26}$: 386.5393. Found: C, 92.68; H, 6.41%. Calcd for $C_{30}H_{26}$: C, 93.51; H, 6.49%.

Rearrangement of 11c. To a solution of **11c** (200 mg, 0.49 mmol) in dioxane (14 mL) was added dropwise 47 wt% hydrobromic acid (5.20 g, 29.7 mmol). After the mixture was stirred at 35 °C for 3 h, ether (50 mL) was added. The organic phase was separated, washed with water (50 mL), dried over anhydrous $MgSO_4$ and evaporated in vacuo, leaving a residue, which, upon recrystallization from benzene, gave **13** (143 mg, 75%) as a colorless solid; mp 202–205 °C; IR (KBr) 2900, 1514, 1492, 1449, 1112, 812, 745 cm^{-1}; ^1H NMR (270 MHz, CD_2Cl_2) δ 1.53–1.63 (m, 3H), 2.44–2.48 (d, J = 9.6 Hz, 2H), 2.50–2.88 (m, 4H), 3.12–3.37 (m, 2H), 6.83–7.01 (m, 4H), 7.04–7.68 (m, 8H), 7.73–7.76 (m, 2H); ^{13}C NMR (67.8 MHz, CD_2Cl_2) δ 20.34, 26.67, 30.04, 35.54, 36.37, 36.84, 41.02, 45.91, 125.51, 125.66, 125.77, 126.49, 126.97, 128.50, 128.96, 129.38, 130.11, 130.78, 130.92, 133.37, 135.09, 135.65, 139.19, 139.35, 139.44; MS (EI) *m/z* 386 (M^+). HRMS Found: 386.5385. Calcd for $C_{30}H_{26}$: 385.5393. Found: C, 93.39; H, 6.90%. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78%.

X-ray Crystal Structure Determination of 11b. Crystal Data : $C_{30}H_{28}O$, MW = 404.52, monoclinic, space group $P2_1/n$, a = 19.742(3) Å, b = 9.2576(6) Å, c = 12.1307(13) Å, β = 104.095(10)°, V = 2150.3(3) Å^3, Z = 4, Dx = 1.248 g cm^{-3}, colorless, prism, crystal size 0.47 × 0.40 × 0.13 mm, $F(000)$ = 281, T = 296(2) K.

Data Collection and Processing: Data were collected on a CAD-4 FR590 diffractometer (software: Enraf-Nonius 1989[11]) using graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å); 5302 reflections collected, 5160 unique reflections were measured, of which 2338 had $I > 2\sigma(I)$.

Structural Analysis and Refinement: MolEN[12] was used for data reduction. The structure was solved by direct methods (SIR 97).[13] SHELXL97[14] was used to refine the structure. $R[F^2 > 2\sigma(F^2)] = 0.0511$; $wR(F^2) = 0.1423$, where $w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 0.0221P]$, where $P = (F_o^2 + 2F_c^2)/3$; $S = 0.982$.

X-ray Crystal-Structure Determination of 11c. Crystal Data: $C_{30}H_{28}O$, MW = 404.52, monoclinic, space group $P2_1/n$, a = 20.2114(15) Å, b = 9.8640(12) Å, c = 11.0511(9) Å, β = 105.775(7)°, V = 2120.9(4) Å^3, Z = 4, Dx = 1.266 g cm^{-3}, colorless, prism, crystal size 0.57 × 0.47 × 0.40 mm, $F(000)$ = 281, T = 296(2) K.

Data Collection and Processing: Data were collected on a CAD-4 FR590 diffractometer (software: Enraf-Nonius 1989[11]) us-

ing graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å); 5241 reflections collected, 5106 Unique reflections were measured, of which 2975 had $I > 2\sigma(I)$.

Structural Analysis: MolEN[12] was used for data reduction. The structure was solved by direct methods (SIR 97).[13] SHELXL97[14] was used to refine the structure. $R[F^2 > 2\sigma(F^2)]$ = 0.0552; $wR(F^2)$ = 0.2065, where $w = 1/[\sigma^2(F_o^2) + (0.1139P)^2 + 0.4672P]$, where $P = (F_o^2 + 2F_c^2)/3$; S = 1.020.

X-ray Crystal Structure Determination of 12a. Crystal Data: The compound crystallized with inclusion of chloroform. Chloroform shows disorder in the crystal. The solvent molecule is omitted in Fig. 3 for reasons of clarity. $C_{29.50}H_{24}Cl_{1.50}$, MW = 431.66, monoclinic, space group $C2/c$, a = 29.301(4) Å, b = 9.4442(19) Å, c = 15.958(3) Å, β = 96.417(3)°, V = 4378.2(13) Å^3, Z = 8, Dx = 1.310 g cm^{-3}, colorless, prism, crystal size 0.25 × 0.20 × 0.15 mm, $F(000)$ = 2048.00, T = 223(2) K.

Data Collection and Processing: Data were collected on a CAD-4 FR590 diffractometer (software: Enraf-Nonius 1989[11]) using graphite-monochromated Cu-$K\alpha$ radiation (λ = 0.71069 Å); 5242 reflections collected, 4958 unique reflections were measured, of which 2317 had $I > 3\sigma(I)$.

Structural Analysis: The structure was solved by direct methods (SIR 92).[15] $R[F^2 > 2\sigma(F^2)]$ = 0.1891; $wR(F^2)$ = 0.5475, where $w = 1/[\sigma^2(F_o^2) + (0.2000P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$; S = 1.716. The large value for the R factor of the structure **12a** can be explained by the disorder of the solvent molecules of chloroform included in the crystal.

X-ray Crystal Structure Determination of 13. Crystal Data: The compound crystallized with the inclusion of dichloromethane. The solvent molecule is omitted in Fig. 4 for reasons of clarity. $C_{30.50}H_{27}Cl$, MW = 428.97, monoclinic, space group $C2$, a = 22.630(4) Å, b = 7.2562(12) Å, c = 13.598(2) Å, β = 90.744(4)°, V = 2232.7(7) Å^3, Z = 4, Dx = 1.276 g cm^{-3}, colorless, prism, crystal size 0.25 × 0.20 × 0.20 mm, $F(000)$ = 908, T = 223(2) K.

Data Collection and Processing: Data were collected on a CAD-4 FR590 diffractometer (software: Enraf-Nonius 1989[11]) using graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71069 Å); 2659 reflections collected, 2659 Unique reflections were measured, of which 2155 had $I > 3\sigma(I)$.

Structural Analysis: The structure was solved by direct methods (SIR 92).[15] $R[F^2 > 2\sigma(F^2)]$ = 0.0624; $wR(F^2)$ = 0.1806, where $w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 2.0569P]$, where $P = (F_o^2 + 2F_c^2)/3$; S = 1.039.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB21 1EZ, UK and copies can be obtained on request, free of charge, by quating the publication citation and the deposition numbers CCDC 176730, 176731, 176732, and 176733. The data are also deposited as Document No. 75016 at the office of the Editor of Bull. Chem. Soc. Jpn.

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