Sequential Rearrangement Reactions of Benzhomonorbornadiene Derivatives: Synthesis of 7-Vinylbenzonorbornadiene

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The reaction of alcohol **12** with $SOCl_2$ gave chlorides **13** and **14**, and the acetolysis of toluene-4-sulfonate **15** gave sequential rearrangement products **16**, **17**, and **18**. In the reaction of **12**, **13** is the major product of sequential rearrangements. Treatment of chloride **13** with *t*-BuOK gave 7-vinylbenzonorbornadiene **19**.

Introduction. – Benzonorbornadiene and its derivatives offer the possibility of several mechanistically interesting investigations. These compounds are intriguing for di-π-methane rearrangement [1], solvolytic reactivity [2], and versatile transformations [3][4]. Among benzonorbornadiene derivatives, halides are generally formed by the addition of halogens to C=C bonds or by conversion of OH derivatives into halides.

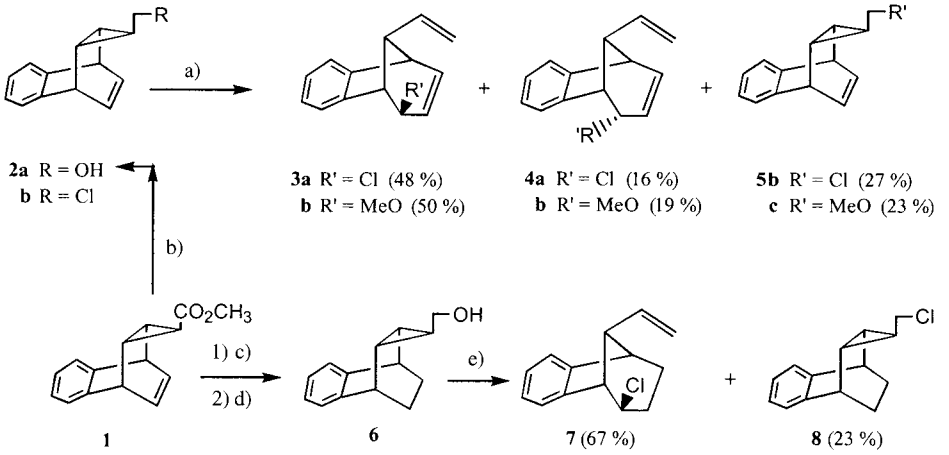
An important method for the synthesis of alkyl chlorides is the reaction of alcohols with reagents such as HCl or $SOCl_2$. The formation of alkyl chlorides as rearranged products depends on both the reaction conditions and reagents used. Strained systems such as cyclopropane, benzonorbornadiene, benzobarrelene, benzhomonorbornadiene, and benzhomobarralene are most likely to undergo rearrangements upon halogenation. Benzhomonorbornadiene and benzhomobarralene systems include a cyclopropane moiety in their structure. The transformation of cyclopropylmethanols into homoallylic halides [5] is a useful reaction and has received considerable attention.

Brominations of benzonorbornadiene, benzobarrelene, and benzhomobarrelene derivatives give both nonrearranged and rearranged products, depending on the reaction conditions [4][6]. As shown in *Scheme 1* [7][8], the reactions of benzhomobarrelene derivatives **2** and **6** give both nonrearranged and rearranged products **3**–**5**, and **7** and **8**, respectively. The rearranged products **3**, **4**, and **7** occur as major products by sequential rearrangements.

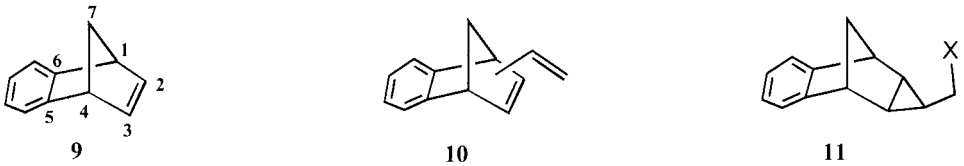
Vinyl groups may be placed at C(1), C(2), or, in *exo*- and *endo*-positions, at C(7) of benzonorbornadienes **9**. These isomers may be important for synthetic and mechanistic studies. Compound **11** may give similar sequential rearrangements, such as that observed for compounds **2** and **6**, because benzhomonorbornadiene derivatives **11** include an annulated cyclopropane ring.

The aim of this study was to obtain a product that can be arrived at by the sequential rearrangement reactions of the benzhomobarrelene systems, and then to synthesize 7-vinylbenzonorbornadiene. Synthesis and the corresponding reactions of dihydrobenzhomobarrelene derivatives were investigated.

Scheme 1



a) $SOCl_2/CHCl_3$ for **2a**; MeO/MeOH, $AgNO_3$ for **2b**. b) $LiAlH_4$; 95%. c) H_2, Pd/C; 100%. d) $LiAlH_4$; 90%. e) $SOCl_2$.

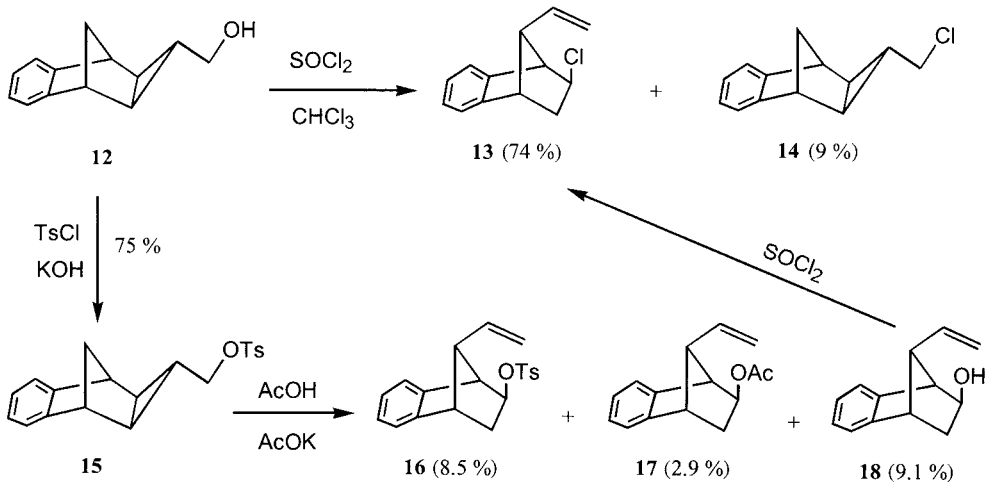


9 **10** **11**

Results and Discussion. – Benzhomonorbornadiene derivative **12** was synthesized as described in [9] and then reacted with $SOCl_2$ in $CHCl_3$ at low temperature for 30 min to give the constitutionally isomeric chlorides **13** and **14** (*Scheme 2*). Nonrearranged **14** could easily be distinguished; it has a symmetrical structure and exhibits an *AA′BB′* system for the aromatic H-atoms in the ^{1}H-NMR spectrum. Also consistent with structure **14** is the eight-line ^{13}C-NMR spectrum. The structure of compound **13** is nonsymmetric and results from the opening of the cyclopropane ring and skeleton rearrangement. There were no signals due to the cyclopropane ring visible in its spectrum. However, signals of a vinyl group were easily discernible. Moreover, it exhibits an *AB* system with *dd* (two *doublets*) and *dt* (*doublet* of *triblets*) for the H-atoms of a CH_2 group. The H-atom in *endo*-position (*trans* to Cl) resonates at 2.14 ppm as a *dd* because it is split into a *dd* by the geminal and the vicinal H-atom, which is located at the C-atom carrying the Cl substituent (*cf.* [4] for comparable examples).

Toluene-4-sulfonate **15** was synthesized for a control experiment. The acetolysis of **15** was undertaken in a 0.09M solution of AcOK in dry AcOH at room temperature for 2 h (*Scheme 2*). In this acetolysis, sequential rearrangement products, namely, toluene-4-sulfonate **16**, acetate **17**, and alcohol **18**, were obtained as pure compounds. Unreacted **15** and nonrearranged products with acetate and OH groups were not observed in this reaction. Examples of solvolysis reactions of cyclopropane derivatives such as acetolysis and ethanolysis have been reported [10]. The NMR spectra of **16**–**18**,

Scheme 2

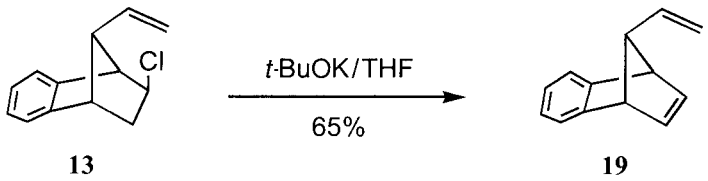


except for TsO, AcO, and OH signals, respectively, are similar to that of chloride **13**. The reaction of alcohol **18** with $SOCl_2$ exclusively gave chloride **13**.

The nonrearrangement product **14** was obtained in a very low yield (9%) in the reaction of **12** with $SOCl_2$, while the nonrearranged products **5b** and **8** are much more prevalent (23–27%) in the reaction of **2a** and **6**, respectively (*Scheme 1*) [7]. Therefore, benzhomonorbornadiene derivative **12** is more strained than benzhomobarrelene derivatives **2a** and **6**.

To synthesize 7-vinylbenzonorbornadiene **19**, the reaction of chloride **13** with *t*-BuOK was investigated (*Scheme 3*). From this reaction, compound **19** was obtained in a yield of 65%. 7-Vinylbenzonorbornadiene **19** could easily be identified; it has a symmetrical structure and exhibits an $AA'BB'$ system for the aromatic H-atoms, and is consistent with an eight-line ^{13}C-NMR spectrum.

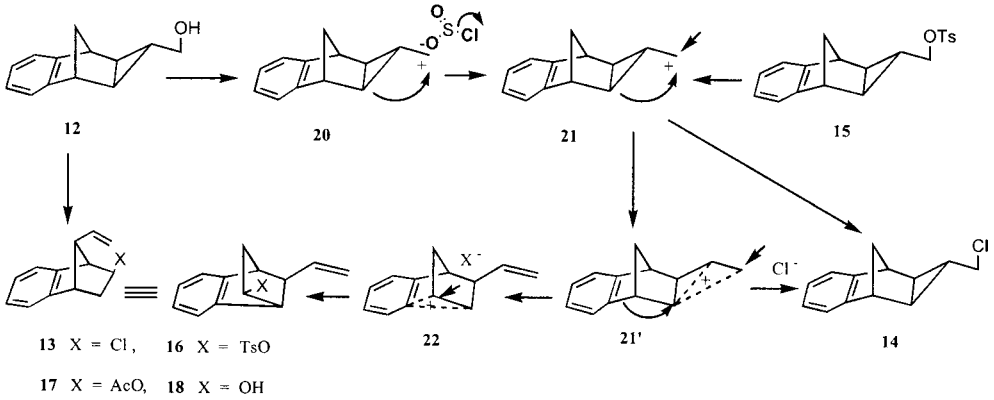
Scheme 3



The following reaction mechanism is proposed in order to rationalize the formation of products **13**, **14**, **16**, **17**, and **18** (*Scheme 4*). Intermediates **20**, **21**, **21′**, and **22** are formed successively from the reaction of compound **12** with $SOCl_2$, with **21**, **21′**, and **22** also being produced by the acetolysis of **15**. Intermediates **21**, **21′**, and **22** are cyclopropylmethyl, homoallyl, and homobenzyl cations, respectively. Alkyl chlorosulfites, which are formed in the reactions of alcohols with $SOCl_2$ to give alkyl halides, react in a two-step process. The first step is the same as the very first step of the S_N1

mechanism, *i.e.* dissociation into an intimate ion pair [11]. Cl^- transferred from $ClSO_2^-$ can attack the intermediate **21** and **21′** to give **14**, and intermediate **22**, to give **13**. In the same way, X^- (TsO^-, AcO^-, or AcOH) can attack **22** to give **16** and **17**. Compound **18** is formed by the hydrolysis of **16** and **17**. As shown in *Scheme 4*, there is a sequential rearrangement in the formation of compounds **13**, **16**, **17**, and **18** by opening the cyclopropane ring in an initial rearrangement, followed by a rearrangement of the benzhomobenzobarrelene skeleton (an aryl shift) as the second rearrangement. An aryl shift is favored over an alkyl shift in this type of system [4][6][7].

Scheme 4



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Experimental Part

General. Column chromatography (CC): silica gel (60 mesh, *Merck*). Prep. thick-layer chromatography (PLC): 1 mm of silica gel *60 PF* (*Merck*) on glass plates. M.p.: *Thomas-Hoover* cap. melting-point apparatus; uncorrected. IR Spectra: from solns. in 0.1-mm cells with a *Perkin-Elmer* spectrophotometer. ^{1}H- and ^{13}C-NMR spectra: 200 (50)-MHz *Varian* spectrometer; δ in ppm, Me_4Si as the internal standard. Elemental analyses: *Carlo Erba 1106* apparatus.

Reaction of anti-*(1*RS*,8*SR*,9*SR*,11*RS*)-Tetracyclo[6.3.1.0^{2,7}.0^{9,11}]dodeca-2,4,6-triene-10-methanol* (**12**) *with* $SOCl_2$. A stirred soln. of **12** (1.2 g, 6.452 mmol) [9] in 20 ml of $CHCl_3$ was cooled to $-10 \pm 5°$ and treated dropwise with a soln. of $SOCl_2$ (8 ml) in 20 ml of $CHCl_3$ for 30 min. Gas evolution was observed. After the addition was complete, the mixture was allowed to warm to r.t. After stirring for 1 day, the solvent and excess $SOCl_2$ were removed by evaporation. The residue was submitted to CC (silica gel (110 g)) eluting with hexane (1. and 2. Fraction).

1. Fraction: anti-*(1*SR*,4*RS*,2*SR*,9*RS*)-2-Chloro-9-ethenyl-1,2,3,4-tetrahydro-1,4-methanonaphthalene* (**13**): 974 mg (74%). Colorless crystals from hexane. M.p. 28–30°. IR ($CHCl_3$): 3080*s*, 3004*s*, 2953*s*, 2927*m*, 2876*m*, 1651*s*, 1472*m*, 1446*w*, 1319*s*, 1268*s*, 1217*m*, 1165*s*, 1012*m*, 987*w*, 757*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.23–7.05 (*m*, 4 arom. H); 6.40 (*ddd*, $^3J_{trans} = 17.22$, $^3J_{cis} = 10.63$, $^3J = 8.26$, C*H*=CH$_2$); 5.22–5.06 (*m*, CH=C*H*$_2$); 3.87 (*ddd*, $^3J = 7.70$, $^3J = 3.72$, $^4J = 1.14$, H–C(2)); 3.49 (br. *s*, H–C(1)); 3.37 (br. *d*, $^3J = 3.37$, H–C(4)); 2.89 (br. *d*, $^3J = 8.26$, H–C(9)); 2.43 (*dt*, *A* of *AB*, $^2J = 13.40$, $^3J = 3.72$, 1 H, CH$_2$); 2.14 (*dd*, *B* of *AB*, $^2J = 13.40$, $^3J = 7.70$, 1 H, CH$_2$). ^{13}C-NMR (50 MHz, $CDCl_3$): 149.64; 147.38; 139.23; 128.71; 128.09; 123.42; 122.99; 118.29; 66.19; 60.49; 59.11; 50.57; 39.60. Anal. calc. for $C_{13}H_{13}Cl$: C 76.28, H 6.40, Cl 17.32; found: C 76.25, H 6.42, Cl 17.30.

2. Fraction: anti-*(1*RS,*8*SR,*9*SR,*11*RS*)-10-(Chloromethyl)tetracyclo[6.3.1.0*^{2,7}*.0*^{9,11}*]dodeca-2,4,6-triene* (**14**): 114 mg (9%). Liquid. IR ($CHCl_3$): 3055*s*, 3029*m*, 3004*w*, 2927*w*, 2876*m*, 1497*s*, 1472*s*, 1421*m*, 1319*s*, 1268*m*, 1140*m*, 1089*s*, 1012*s*, 936*m*, 859*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.20–7.17 (*AA′* of *AA′BB′*, 2 arom. H); 7.05–7.00 (*BB′* of *AA′BB′*, 2 arom. H); 3.63 (*d*, ^3J = 7.41, CH_2Cl); 3.38 (br. *s*, H–C(1), H–C(8)); 2.25 (*tt*, ^3J = 7.41, ^3J = 2.53, H–C(10)); 1.55 (*d*, *A* of *AB*, ^2J = 10.13, 1 H–C(12)); 1.32 (*d*, *B* of *AB*, ^2J = 10.13, 1 H–C(12)); 1.13 (*d*, ^3J = 2.53, H–C(9), H–C(11)). ^{13}C-NMR (50 MHz, $CDCl_3$): 152.44; 127.08; 122.85; 48.73; 45.03; 40.86; 32.20; 30.94. Anal. calc. for $C_{13}H_{13}Cl$: C 76.28, H 6.40, Cl 17.32; found: C 76.31, H 6.41, Cl 17.33.

Reaction of **12** *with TsCl.* Alcohol **12** (1.998 g, 10.742 mmol) and 2.16 g (11.339 mmol) of TsCl were dissolved in 60 ml of dry Et_2O in a 100-ml flask equipped with a drying tube and magnetic stirrer. The soln. was colled to $-10 \pm 5°$, and portions of powdered KOH (2.5 g, 44.643 mmol) were added over a period of 2 h. The mixture was stirred at 0° for 20 h. The mixture was poured into 75 g of ice and stirred for 15 min. The Et_2O layer was separated, and the aq. layer was extracted with Et_2O (2 × 100 ml). The combined org. layer was washed with H_2O (100 ml) and dried (Na_2SO_4). The solvent was removed, and then the residue was crystallized from hexane/$CHCl_3$.

anti-*(1*RS,*8*SR,*9*SR,*11*RS*)-Tetracyclo[6.3.1.0*^{2,7}*.0*^{9,11}*]dodeca-2,4,6-triene-10-methyl Toluene-4-sulfonate* (**15**): 2.752 g (75%). Colourless crystals. M.p. 78–80°. IR ($CHCl_3$): 2926*w*, 1618*m*, 1474*m*, 1421*s*, 1367*m*, 1313*s*, 1259*m*, 1188*s*, 1098*s*, 955*m*, 865*m*, 829*s*, 758*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.78 (*d*, *A* of *AB*, ^3J = 8.20, 2 arom. H); 7.32 (*d*, *B* of *AB*, ^3J = 8.20, 2 arom. H); 7.20–7.14 (*AA′* of *AA′BB′*, 2 arom. H); 7.07–7.01 (*BB′* of *AA′BB′*, 2 arom. H); 3.83 (*d*, ^3J = 7.43, CH_2OTs); 3.28 (*s*, H–C(1), H–C(8)); 2.46 (*s*, Me); 2.13 (*tt*, ^3J = 7.43, ^3J = 2.51, H–C(10)); 1.42 (*d*, *A* of *AB*, ^2J = 10.05, 1 H–C(12)); 1.26 (*d*, *B* of *AB*, ^2J = 10.05, 1 H–C(12)); 1.00 (br. *d*, ^3J = 2.51, H–C(9), H–C(11)). ^{13}C-NMR (50 MHz, $CDCl_3$): 152.52; 146.68; 135.46; 131.82; 129.86; 127.09; 122.89; 74.36; 44.75; 40.77; 28.84; 28.10; 23.62. Anal. calc. for $C_{20}H_{20}O_3S$: C 70.56, H 5.92, S 9.42; found: C 70.60, H 5.90, S 9.41.

Acetolysis of **15**. Compound **15** (1.071 g, 3.15 mmol) was taken up in 40 g of a 0.09M soln. of AcOK in dry AcOH. The soln. was allowed to stand for 2 h at r.t. H_2O (400 ml) was added, and then the mixture was extracted with $CHCl_3$ (3 × 50 ml). These $CHCl_3$ extracts were washed with aq. $NaHCO_3$ (5%, 50 ml) and H_2O (50 ml), resp., and then dried ($CaCl_2$). After removing the solvent, the residue was submitted to PLC with AcOEt/hexane 3:7. Compounds **16** (90 mg, m.p. 104–106°, colourless crystals from $CHCl_3$, 8.5%), **17** (21 mg, liquid, 2.9%), and **18** (35 mg, liquid, 9.1%) were isolated in pure state.

*(1*SR,*4*RS,*2*SR,*9*RS*)-9-Ethenyl-1,2,3,4-tetrahydro-1,4-methanonaphthalen-2-yl Toluene-4-sulfonate* (**16**): IR ($CHCl_3$): 3055*m*, 3004*s*, 1957*s*, 1927*s*, 1600*w*, 1472*s*, 1370*w*, 1217*s*, 1114*w*, 1012*s*, 961*m*, 885*s*, 757*w*. ^{1}H-NMR (200 MHz): 7.77 (*d*, *A* of *AB*, ^3J = 8.17, 2 arom. H); 7.34 (*d*, *B* of *AB*, ^3J = 8.17, 2 arom. H); 7.19–6.98 (*m*, 4 arom. H); 6.13 (*ddd*, $^3J_{trans}$ = 17.56, $^3J_{cis}$ = 10.83, ^3J = 8.28, C*H*=CH$_2$); 5.13 (*dd*, $^3J_{cis}$ = 10.83, ^4J = 1.04, (*Z*)-H of CH=C*H*$_2$); 5.09 (*dd*, $^3J_{trans}$ = 17.56, ^4J = 1.04, (*E*)-H of CH=C*H*$_2$); 4.50 (*dd*, ^3J = 7.29, ^3J = 2.81, H–C(2)); 3.80 (br. *s*, H–C(1)); 3.30 (*m*, H–C(4)); 2.84 (br. *d*, ^3J = 8.28, H–C(9)); 2.47 (*s*, Me); 2.14 (*dt*, *A* of *AB*, ^2J = 13.42, ^3J = 3.41, 1 H–C(3)); 1.85 (*dd*, *B* of *AB*, ^2J = 13.42, ^3J = 7.29, 1 H–C(3)). ^{13}C-NMR (50 MHz, $CDCl_3$): 150.53; 146.21; 144.80; 138.51; 136.69; 131.69; 129.87; 128.83; 128.14; 124.26; 122.81; 118.92; 85.15; 66.08; 55.92; 49.54; 36.33; 23.65. Anal. calc. for $C_{20}H_{20}O_3S$: C 70.56, H 5.92, S 9.42; found: C 70.55, H 5.91, S 9.44.

*(1*SR,*4*RS,*2*SR,*9*RS*)-9-Ethenyl-1,2,3,4-tetrahydro-1,4-methanonaphthalen-2-yl Acetate* (**17**): IR ($CHCl_3$): 3080*m*, 3029*m*, 2978*w*, 2927*w*, 1753*w*, 1651*w*, 1472*s*, 1446*s*, 1395*w*, 1268*w*, 1165*w*, 1038*m*, 987*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.26–7.02 (*m*, 4 arom. H); 6.19 (*ddd*, $^3J_{trans}$ = 16.18, $^3J_{cis}$ = 10.24, ^3J = 8.49, C*H*=CH$_2$); 5.14 (*dd*, $^3J_{trans}$ = 16.18, ^4J = 1.10, (*E*)-H of CH=C*H*$_2$); 5.07 (*dd*, $^3J_{cis}$ = 10.24, ^4J = 1.10, (*Z*)-H of CH=C*H*$_2$); 4.71 (*dd*, ^3J = 7.29, ^3J = 3.27, H–C(2)); 3.94 (br. *s*, H–C(1)); 3.28 (br. *d*, ^3J = 2.03, H–C(4)); 2.86 (br. *d*, ^3J = 8.49, H–C(9)); 2.13–1.91 (*m*, CH_2); 2.07 (*s*, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 172.01 (CO); 150.62; 145.89; 139.35; 128.44; 127.94; 124.11; 122.65; 118.20; 78.34; 66.06; 55.58; 49.79; 36.11; 23.15. Anal. calc. for $C_{15}H_{16}O_2$: C 78.92, H 7.06; found: C 78.90, H 7.05.

*(1*SR,*4*RS,*2*SR,*9*RS*)-9-Ethenyl-1,2,3,4-tetrahydro-1,4-methanonaphthalen-2-ol* (**18**): IR ($CHCl_3$): 3490*w*, 3055*w*, 2412*m*, 1548*w*, 1497*w*, 1421*w*, 1242*s*, 1063*s*, 936*m*, 757*w*, 680*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.18–7.01 (*m*, 4 arom. H); 6.33 (*ddd*, $^3J_{trans}$ = 17.58, $^3J_{cis}$ = 10.45, ^3J = 6.92, C*H*=CH$_2$); 5.18 (br. *d*, $^3J_{trans}$ = 17.58, (*E*)-H of CH=C*H*$_2$); 5.14 (br. *d*, $^3J_{cis}$ = 10.45, (*Z*)-H of CH=C*H*$_2$); 3.93 (*dd*, ^3J = 6.67, ^3J = 3.48, H–C(2)); 3.31 (*m*, H–C(1), H–C(4)); 2.87 (br. *d*, ^3J = 6.92, H–C(9)); 2.03–1.87 (*m*, CH_2, OH). ^{13}C-NMR (50 MHz, $CDCl_3$): 150.77; 146.94; 140.31; 128.09; 127.67; 123.58; 122.64; 118.39; 77.17; 65.19; 58.60; 49.26; 38.99. Anal. calc. for $C_{13}H_{14}O$: C 83.83, H 7.58; found: C 83.85, H 7.58.

Reaction of **18** *with* $SOCl_2$. To a soln. of **18** (33 mg) in 0.5 ml of $CDCl_3$ (in NMR tube) was added $SOCl_2$ (excess). Gas evolution was observed. After 2 h, the NMR spectrum of the mixture was checked. It showed that **18** was completely converted into **13**.

Treatment of **13** *with* t-*BuOK*. To a stirred soln. of **13** (300 mg, 1.143 mmol) in dry THF (30 ml) was added *t*-BuOK (4.0 g, 35.714 mmol) at r.t. The mixture was stirred for 6 d. After evaporation of the solvent, H_2O (30 ml) was added. The mixture was neutralized with NH_4Cl (solid) and extracted with $CHCl_3$ (3×30 ml). The combined org. layer was washed with H_2O (50 ml) and dried ($CaCl_2$). After evaporation of the solvent, **19** was obtained as a liquid (128 mg, 65%).

anti-*(1*SR,*4*RS*)-9-Ethenyl-1,4-tetrahydro-1,4-methanonaphthalene* (**19**): IR ($CHCl_3$): 3083*m*, 3052*m*, 3021*s*, 2990*m*, 2918*m*, 1566*s*, 1459*s*, 1416*s*, 1308*s*, 1286*s*, 1179*m*, 1157*m*, 1093*s*, 985*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.23–7.17 (*AA′* of *AA′BB′*, 2 arom. H); 6.96–6.90 (*BB′* of *AA′BB′*, 2 arom. H); 6.65 (*t*, $^3J = 1.95$, 2 olef. H); 6.04 (*ddd*, $^3J_{trans} = 17.36$, $^3J_{cis} = 10.40$, $^3J = 7.78$, 1 olef. H); 5.07 (*dd*, *A* of *AB*, $^3J_{trans} = 17.36$, $^2J = 2.01$, (*E*)-H of CH=CH_2; 5.03 (*dd*, *B* of *AB*, $^3J_{cis} = 10.40$, $^2J = 2.01$, (*Z*)-H of CH=CH_2); 3.81–3.75 (*m*, H–C(1), H–C(4)); 3.26 (br. *d*, $^3J = 7.78$, H–C(9)). ^{13}C-NMR (50 MHz, $CDCl_3$): 153.80; 141.56; 139.74; 126.21; 123.31; 119.05; 87.20; 57.13. Anal. calc. for $C_{13}H_{12}$: C 92.81, H 7.19; found: C92.80, H 7.20.

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