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Sequential Rearrangements and Unusual Isomerization with KO^{t}Bu: Synthesis of *anti*-12-Vinyltricyclo[6.3.1.0^{2,7}]-dodeca-2,4,6,9-tetraene and its Derivatives

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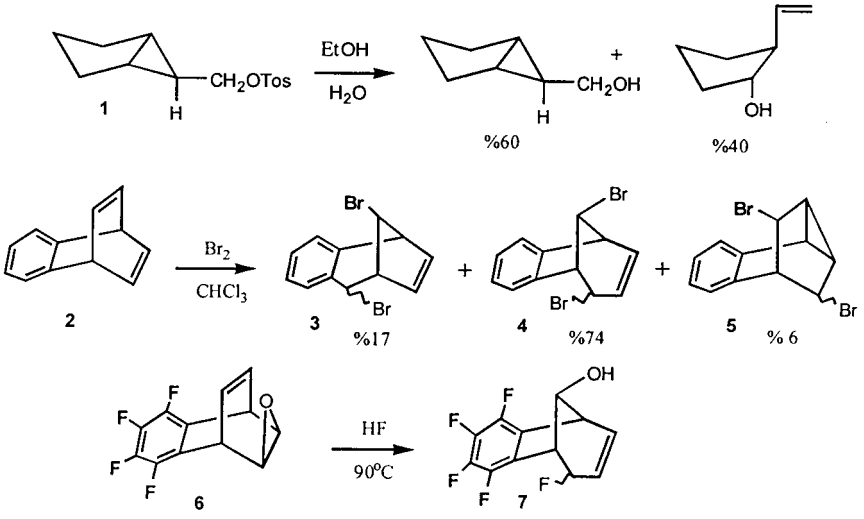
Abstract—The reaction of alcohol **13a** with $SOCl_2$ gave **13b**, **14a** and **15a**, and the reaction of chloride **13b** with $AgNO_3$ (in MeO^-/MeOH) gave **13c**, **14b** and **15b**. In these reactions, **14a**, **14b**, **15a** and **15b** are the major products by sequential rearrangements. Treatment of the rearranged products **14a** and **15a** with KO^{t}Bu (potassium *tert*-butoxide) gave **18** by an unusual isomerization. Compounds **19**, **20** and **21** were also synthesized in different reactions. Compounds **14**, **15**, **19**, **20** and **21** are all derivatives of anti-12-vinyltricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene **19**, and the syntheses of **19**, **20** and **21** support the structures of compounds **14**, **15** and **18**.

Introduction

An important method for the synthesis of alkyl chlorides is the reaction of alcohols with reagents such as HCl and thionyl chloride. The formation of alkyl chlorides as rearranged products depends on both the reaction conditions and reagents used. Strained systems are most likely to produce rearrangements. Cyclopropane, benzobarrelene (**2**) and benzhomobarrelene systems are all strained, with benzhomobarrelene including both cyclopropane and benzobarrelene structures, and these compounds rearrange to give some interesting products. The transformation of cyclopropylmethanols into homoallylic halides[1–5] is a useful reaction which has received considerable attention. The solvolysis of annulated cyclopropane derivatives such as bicyclo[*n*.1.0]hexane **1** or pentane tosylates gives two different products, one of which is rearranged and the other non-rearranged[6] (Scheme 1). Bromination of



Scheme 1.

Keywords: cyclopropanes; isomerisation; rearrangements.

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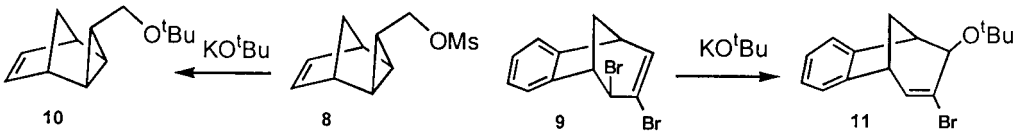


Scheme 2.

benzobarrelene[7] (**2**) at 10°C provided isomeric dibromides **3**, **4** and **5** with rearranged skeletons. The reaction of tetrafluorobenzobarreleneoxide **6** with HF at 90°C gave the alcohol **7** by successive rearrangements.[8]

KO^{t}Bu (potassium *tert*-butoxide) reacts with alkyl halogens to give the corresponding alkenes by dehydrohalogenation. In some cases, KO^{t}Bu reacts with alkyl halogens to give alkyl ethers by the S_N2 or S_N2' mechanism. For example, alkyl mesylate **8**[9] and dibromide **9**[10] react with KO^{t}Bu to give the corresponding ethers **10** and **11**, respectively (Scheme 2).

Bromination of benzhomobarrelene derivatives[11] **12** (Scheme 3), which contain barrelene skeletons where a double bond is blocked by a cyclopropane ring, at low temperatures give both non-rearranged and rearranged products. For some products, the skeleton alone was rearranged, protecting the cyclopropane rings.

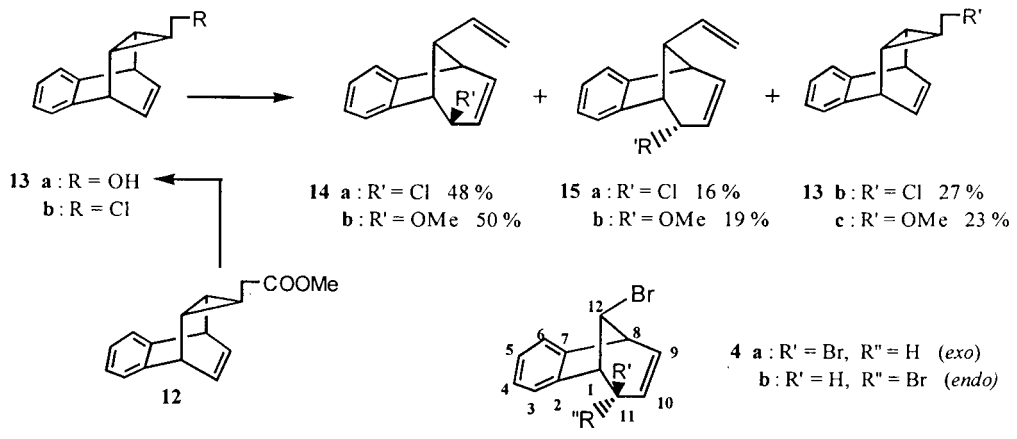
The aim of this study was to synthesize *anti*-12-vinyltricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene and its derivatives (ring system of **7**, Scheme 1, with vinyl in the place of OH). The rearrangement reactions of benzhomobarrelene derivatives and the elimination and reduction reactions of the products formed with $SOCl_2$ were also investigated.

Results and Discussion

Benzhomobarrelene derivative **12** was synthesized as described in the literature[12,13] and reduced with $LiAlH_4$ to give alcohol **13a**. Benzhomobarrelene derivative **13a** was reacted with $SOCl_2$ in $CHCl_3$ at room temperature for 3 h to give the isomeric chlorides **13b**, **14a** and **15a** (Scheme 3). Non-rearranged **13b** could easily be distinguished; it has a symmetrical structure and exhibits an AA′BB′ system for aromatic protons, and is consistent with the eight-line ^{13}C NMR spectrum seen. According to the NMR spectra of compounds **14a** and **15a**, they were asymmetric and rearranged products resulting from opening the cyclopropane ring and transforming the [2.2.2] system into a [3.2.1] system. There were no peaks due to cyclopropane rings visible in either of their spectra, but those from two double bonds were seen, of which one was vinylic (Fig. 1). In the same way, benzhomobarrelene derivative **13b** reacted with MeONa/MeOH in the presence of the catalyst $AgNO_3$ to give **13c**, **14b** and **15b** (Scheme 3).

The ^1H NMR spectra of compounds **14** and **15** are very similar to the *exo* and *endo* forms of **4**.[7] In **14** and **15**, there are vinyl groups at the C-12 carbon atoms and Cl and OMe at the C-11 carbon atoms, instead of the bromine atoms in those positions in compound **4**. The configurations of Cl and OMe at the C-11 carbon atoms in **14** and **15** were determined by examining the γ gauche effect[14–16] and coupling constants. The protons at the C-11 carbon atoms resonate at 4.52, 3.50, 4.89 and 3.94 ppm in **14a**, **14b**, **15a** and **15b**, respectively. The *exo* protons in **15** resonate at lower fields than the *endo* protons in **14** due to the strong steric repulsion between the proton and the vinyl group in **15**. These protons show as a multiplet, although this does not indicate the presence of any measurable coupling constants besides the the line broadening, with **14** showing more broadening than **15**. Thus, the configurations of Cl and OMe in **14** and **15** are *exo* for **14** and *endo* for **15**.

To confirm the structural assignments of compounds **14a** and **15a** and to obtain those for **19** and its new derivatives, some additional chemical reactions were investigated (Scheme 4). Treatment of the rearranged products **14a** and **15a**, either as pure isomers or a mixture of the two, with KO^{t}Bu gave isomeric product **18** (Fig. 1). The reaction of KO^{t}Bu with allylic bromide in the bicyclic [3.2.1] system



Scheme 3.

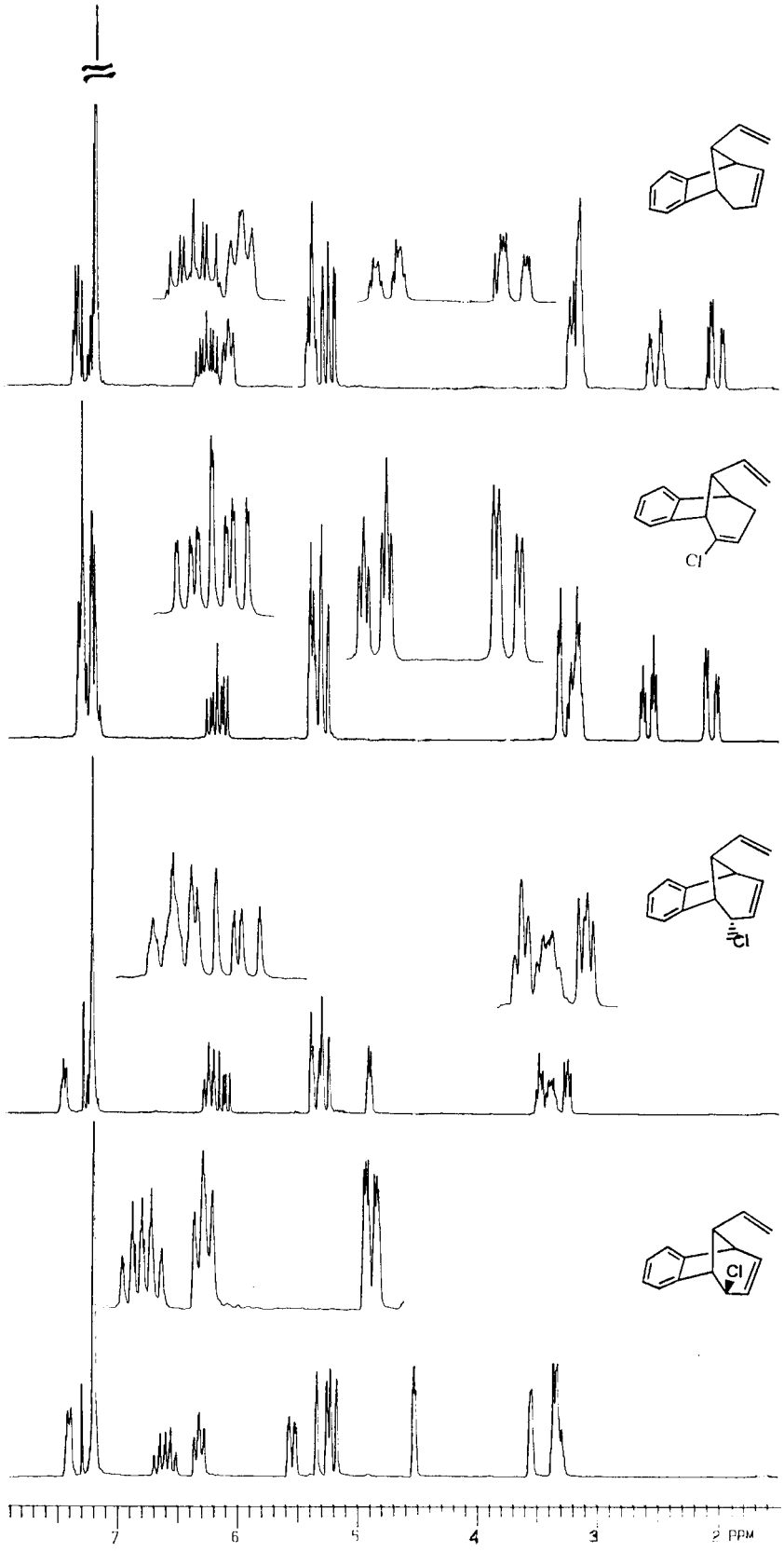
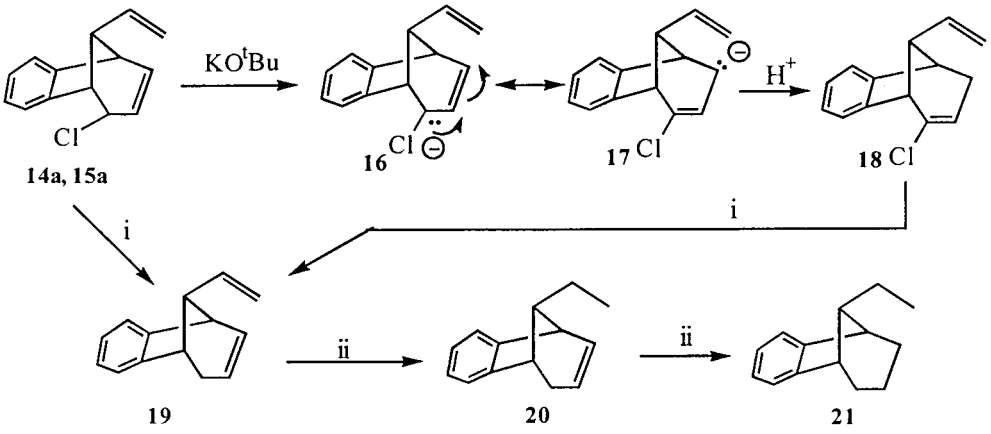
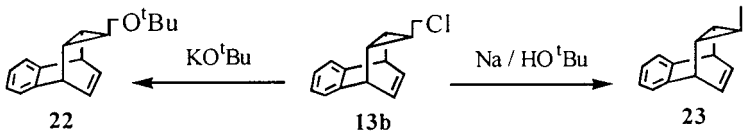


Fig. 1. 200 MHz ^{1}H-NMR spectra of **14a, 15a, 18** and **19**.



Scheme 4. i=Na, *tert*-butanol/ether; ii=H_2/Pd-C, EtOAc.

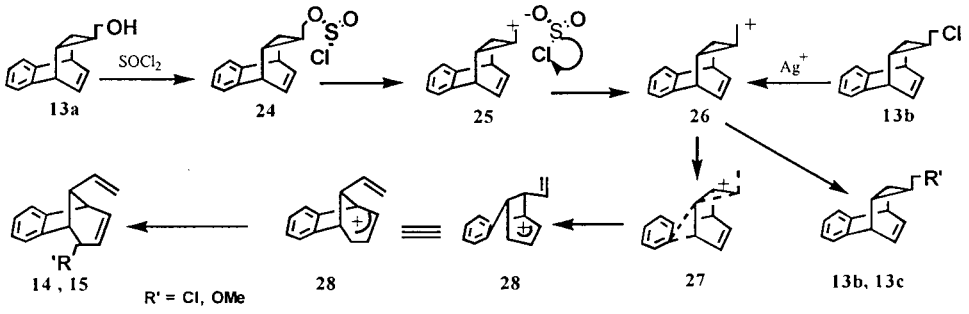


Scheme 5.

gives an allylic substituted product.[10] In order for substitution in **14a** and **15a** to occur by S_N2 while KO^{t}Bu (a base) attacks the CHCl *endo* or *exo* sides, the chlorine atoms must leave. The mechanism involves deprotonation to give **16/17** and then subsequent protonation to give vinyl chloride **18**. Isomerization of **14a** is faster than that of **15a** because KO^{t}Bu approaches CHCl more slowly from the *exo* side due to the steric effect of the vinyl group. These reactions highlight the configurations of the chlorine atoms in **14a** and **15a**. When reductive dehalogenation reactions of chlorine atoms in the pure isomers of **14a**, **15a** and **18** were studied, it was observed that all of them gave the same product **19** (Scheme 4, Fig. 1). Hydrogenation of **19** gave the unsaturated and saturated aromatic hydrocarbons **20** and **21**. Further investigation revealed that compound **19** is reduced via **20** to **21**.

To compare the effects of KO^{t}Bu with Na/HO^{t}Bu, the reactions of benzhomobarrelene derivative **13b** were also studied (Scheme 5). The reactions of **13b** with KO^{t}Bu and Na/HO^{t}Bu gave substitution products **22** and **23**, respectively. For the formation of **22**, the proposed mechanism may be α-deprotonation followed by carbenoid elimination and addition. However, Stampfli et al.[9] reported the absence of the elimination-addition mechanism in the reaction of **8** with $^-$O^{t}Bu (Scheme 2). Although bromine attacks more from exo-face of π-system in **4**,[7] it and *m*-chloroperbenzoic acid could not attack from this face in **12**[11] due to steric effects associated with adjacent cyclopropane and double bond. It can be accepted that KO^{t}Bu could not approach the proton closely enough for dehydrochlorination due to steric effect. Therefore, the substitution by S_N2 can be proposed as another mechanism

The following reaction mechanism is proposed in order to rationalise the formation of products **13b**, **13c**, **14** and **15** (Scheme 6). Intermediates **24**, **25** and **26**, successively, are formed from the reaction of compound **13a** with thionyl chloride, with **26** also being produced by the reaction of **13b** with $AgNO_3$. Alkyl chlorosulfites, which are formed in the reactions of alcohols with thionyl chloride 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—dissociation into an intimate ion pair.[17,18] Alkyl halogens can react with $AgNO_2$ or $AgNO_3$ by either an S_N1 or S_N2 mechanism, depending on the reaction conditions,[19–21] as



Scheme 6.

even primary halogens have been reported to undergo S_N1 reactions when assisted by metal ions. Intermediate **26** is converted into **28** through an intermediate **27** by opening the cyclopropane ring in an initial rearrangement, followed by a rearrangement of the benzobarrelene skeleton, an aryl shift, as the second rearrangement. An aryl shift is favored over an alkyl shift in this type of system.[7,22–24] Cl^- transferred from $ClSOO^-$, or MeO^-, can attack both the intermediate **26**, to give **13** (**b** and **c**), and the intermediate **28** at different positions, to give **14** and **15**.

Experimental

Melting points were determined using a Thomas–Hoover capillary melting apparatus and are uncorrected. Infrared spectra were obtained from solutions in 0.1 mm cells with a Perkin–Elmer spectrophotometer. The ^1H- and ^{13}C NMR spectra were recorded on a 200 (50)-MHz Varian spectrometer and reported in units, with $Si(Me_3)_4$ as the internal standard. Mass spectra were determined on VG ZabSpec, double focusing, magnetic sector (100.000 resolution) Max. range 1000 for EI, 10000 for HRMS. Elemental analyses were performed on carlo Erba 1106 apparatus. All column chromatography was performed on silica gel (60-mesh, Merck). PLC is preparative thick-layer chromatography: 1 mm of silica gel 60 PF (Merck) on glass plates. Column chromatography (CC) was carried out on silica gel 60–200 (Merck).

Reduction of 12 with $LiAlH_4$. To a stirred solution of **12** (678 mg, 3 mmol) in dry tetrahydrofuran (THF) (30 mL) was added $LiAlH_4$ (100 mg, 2.8 mmol), in portions over a period of 15 min, at 0°C. After stirring at the same temperature, the reaction mixture was allowed to stand for 5 h at room temperature. The gray was returned to 0°C, and hydrolyzed by the addition of methanol and water (1:1). The mixture was filtered (inorganic salts) and the solvent evaporated. The residue was cooled to 0°C, was added $CHCl_3$ (50 mL), and the solution was washed with a solution of NH_4Cl (5%, 20 mL) and water (20 mL), dried over Na_2SO_4 and the solvent was evaporated, to leave the alcohol **13a** (564 mg; 95%) as a colourless viscous liquid. δ_H (200 MHz, $CDCl_3$) 7.26–7.20 (AA′ part of AA′BB′-system, aromatic, 2H), 7.18–7.04 (BB′ part of AA′BB′-system, aromatic, 2H), 6.22 (m, olefinic, 2H), 4.27 (m, bridgehead, 2H), 3.47 (d, J=7.1 Hz, C*H*$_2$OH, 2H), 1.70 (bs, OH, 1H), 1.58–1.48 (m, cyclopropane, 1H), 1.22 (m, cyclopropane, 2H); δ_C (50 MHz, $CDCl_3$) 148.9 (C), 134.0 (CH), 126.7 (CH), 125.1 (CH), 66.1 (CH_2), 43.1 (CH), 31.7 (CH), 24.7 (CH); ν_{max} (liquid film) 3617, 3438, 3029, 2978, 2927, 2876, 1472, 1421, 1370, 1217, 1038 cm^{-1}; HRMS: found 198.1042, calc for $C_{14}H_{14}O$ 198.1044.

Reaction of alcohol 13a with $SOCl_2$

To a stirred solution of alcohol **13a** (620 mg, 3,37 mmol) in $CHCl_3$ (20 mL) was immediately added $SOCl_2$ (5 mL), at room temperature. Gas evolution was observed. After stirring for 3 h, the solvent and excess $SOCl_2$ were removed by evaporation. The residue was submitted to column chromatography (silica gel, 45 g) eluting with hexane.

1. Fraction: *anti*, *exo*-11-chloro-12-vinyltricyclo-[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene (14a). (350 mg, 48%) mp 73–75°C as colourless crystals from hexane; δ_H (200 MHz, $CDCl_3$) 7.38–7.15 (m, aromatic, 4H), 6.58 (dddd, J=7.9, 1.5, 17.1, 10.4 Hz, olefinic, 1H), 6.30 (bdd, A part of AB-system, J=9.6, 8.0 Hz, olefinic 1H), 5.53 (bdm, B part of AB-system, J=9.6 Hz, olefinic, 1H), 5.29 (bd, J=17.1 Hz, olefinic, 1H), 5.19 (bd, J=10.4 Hz, olefinic, 1H), 4.52 (m, Cl–C*H*, 1H), 3.54 (m, 1H), 3.36–3.30 (m, 2H); δ_C (50 MHz, $CDCl_3$) 154.1 (C), 145.7 (C), 140.0 (CH), 136.5 (CH), 128.9 (CH), 128.5 (CH), 127.5 (CH), 126.7 (CH), 123.3 (CH), 118.2 (CH_2), 58.1 (CH), 55.4 (CH), 54.2 (CH), 46.9 (CH); ν_{max} ($CHCl_3$) 3105, 3029, 2978, 2898, 1627, 1455, 1379, 1231, 798, 751, 702 cm^{-1}; *m*/*z* 218/217/216/215 (8/8/20/10), 182/181/180/179 (18/100/40/23), 167/166/165 (21/26/34), 154/153 (15/15), 141 (23), 128 (17); HRMS: found 216.0704, calc for $C_{14}H_{13}{}^{35}Cl$ 216.0705.

2. Fraction: *anti*, *endo*-11-chloro-12-vinyltricyclo-[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene (15a). (115 mg, 16%) as liquid: δ_H (200 MHz, $CDCl_3$) 7.46–7.15 (m, aromatic, 4H), 6.26–6.05 (m, olefinic, 2H), 5.37–5.23 (m, olefinic, 3H), 4.89 (m, Cl–C*H*, 1H), 3.48 (t, J=4.8 Hz, bridgehead, C*H*CHCl, 1H), 3.40 (m, bridge, 1H), 3.25 (dd, J=3.7, 6.3 Hz, =CHC*H*, bridgehead, 1H); δ_C (50 MHz, $CDCl_3$) 153.8 (C), 143.3 (C), 137.9, 135.3, 129.5, 129.0, 127.9, 127.3, 122.7, 120.2, 60.1 (CH), 57.9 (CH), 54.1 (CH), 50.0 (CH); ν_{max} ($CHCl_3$) 3140, 2986, 2926, 1641, 1643, 1410, 1194, 921, 740, 647 cm^{-1}; *m*/*z* 218/217/216/215 (8/5/25/7), 197 (5), 182/181/180/179/178/177 (18/100/24/27/26), 167/166/165 (29/45/75), 153/152 (33/37), 141/139 (40/14), 128 (53), 115 (37), 63 (24). HRMS: found 216.0702 calc for $C_{14}H_{13}{}^{35}Cl$ 216.0705.

3. Fraction: *anti*, *exo*-10-chloromethyl-tetracyclo-[6.3.2.0^{2,7}.0^{9,11}]tetradeca-2,4,6,12-tetraene (13b). (194 mg, 27%) mp 49–50°C as colourless crystals from hexane; δ_H (200 MHz, $CDCl_3$) 7.24–7.17 (AA′ part of AA′BB′-system, aromatic, 2H), 7.10–7.04 (BB′ part of AA′BB′-system, aromatic, 2H), 6.22 (m, olefinic, 2H), 4.07 (m, bridgehead, 2H), 3.43 (d, J=7.6 Hz, C*H*$_2$Cl, 2H), 1.62 (tt, J=7.6, 3.0 Hz, cyclopropane, 1H), 1.30 (m, cyclopropane, 2H); δ_C (50 MHz, $CDCl_3$) 148.5 (C), 133.9 (CH), 126.8 (CH), 125.1 (CH), 48.8, 43.0, 31.2, 27.2; ν_{max} ($CHCl_3$) 3085, 2926, 1477, 1411, 1361, 1313, 1268, 1225, 1143, 1106, 1071, 1005, 945, 756, 705 cm^{-1}. Anal. Calcd For $C_{14}H_{13}Cl$: C, 77.59; H, 6.05. Found: C, 77.50; H, 6.03.

Treatment of *exo*-chloride 14a with KO^{t}Bu

To a stirred solution of *exo*-chloride **14a** (350 mg, 1,6 mmol) in dry THF (15 mL) was added KO^{t}Bu (potassium *tert*-butoxide, 600 mg, 5.36 mmol) at room temperature. The mixture was stirred for 1.5 days. After evaporation of the solvent, water (100 mL) was added. The mixture was extracted with ether (3×50 mL). The combined organic layer was dried over $CaCl_2$ and the solvent was evaporated. Tetraene **18** was obtained as a pale yellow liquid (300 mg, 85%).

***anti*-9-Chloro-12-vinyltricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene (18).** δ_H (200 MHz, $CDCl_3$) 7.30–7.11 (m,

aromatic, 4H), 6.15 (dddd, J=17.5, 10.2, 7.0, 1.1 Hz, olefinic, 1H), 5.38–5.23 (m, olefinic, 3H), 3.17 (d, J=3.7 Hz, 1H), 3.25–3.13 (m, 2H), 2.57 (ddd, J=18.0, 3.4, 3.6 Hz, A part of AB-system, methylenic, 1H), 2.05 (bdd, J=18.0, 4.2 Hz, B part of AB-system, methylenic, 1H); δ_C (50 MHz, $CDCl_3$) 151.4 (C), 147.8 (C), 138.3 (CH), 135.9 (C), 129.0 (CH), 128.5 (CH), 125.3 (CH), 122.8, (CH), 121.6 (CH), 119.7 (CH_2), 55.6 (CH), 54.9 (CH), 45.0 (CH), 31.4 (CH_2); ν_{max} ($CHCl_3$) 3105, 2926, 2836, 1666, 1477, 1424, 1322, 1000, 913, 813, 733 cm^{-1}; m/z 218/217/216/215 (20/17/61/22), 197 (27), 181/180/179/178/175 (100/31/34/23/22), 167/166/165 (27/52/77), 153/152 (34/37), 141/139 (28/116), 128 (29), 115 (25), 63 (9); HRMS: found 216.0706, calc for $C_{14}H_{13}{}^{35}Cl$ 216.0705.

Treatment of *endo*-chloride 15a with KO^{t}Bu

To a stirred solution of *endo*-chloride **15a** (230 mg, 1.06 mmol) in dry THF (15 mL) was added KO^{t}Bu (2 g, 17.86 mmol) at room temperature. The mixture was stirred for 5 days. The other parts of the reaction were studied in the same manner as the *exo*-chloride **14a**, and tetraene **18** was obtained as 200 mg, (87%).

Treatment of *exo*- and *endo*-chlorides 14a and 15a with KO^{t}Bu

A mixture (885 mg) of *exo*- and *endo*-chlorides **14a** and **15a** (77:23) was dissolved in dry THF (50 mL). To this solution was added KO^{t}Bu (2 g, 17.86 mmol) at room temperature. The mixture was stirred for 4 days. The other parts of the reaction were studied in the same manner as the *exo*-chloride **14a**. ^{1}H NMR analysis of the reaction mixture indicated the presence of *endo*-chloride **15a** in addition to tetraene **18**, and the absence of *exo*-chloride **14a**.

Treatment of chloride 13b with KO^{t}Bu

To a stirred solution of chloride **13b** (190 mg, 0.87 mmol) in dry THF (15 mL) was added KO^{t}Bu (1.5 g, 13.04 mmol) at room temperature. The mixture was refluxed for 3 days and then cooled to room temperature. The other parts of the reaction were studied in the same manner as the *exo*-chloride **14a**, and substituted product **22** was obtained as 158 mg (71%).

***anti*, *exo*-Tetracyclo[6.3.2.0^{2,7}.0^{9,11}]tetradeca-2,4,6,12-tetraene-10-yl-*tert*-butoxymethane (22).** δ_H (200 MHz, $CDCl_3$) 6.94–6.88 (AA′ part of AA′BB′-system, aromatic, 2H), 6.80–6.74 (BB′ part of AA′BB′-system, aromatic, 2H), 5.94 (m, olefinic, 2H), 3.76 (m, bridgehead, 2H), 2.94 (d, J=6.7 Hz, CH_2(CH_3)$_3$, 2H), 1.22–1.03 (m, cyclopropane, 3H), 0.91 (s, CH_2(CH_3)$_3$, 9H); δ_C (50 MHz, $CDCl_3$) 149.1 (C), 133.9 (CH), 126.5 (CH), 124.9 (CH), 74.4 (C), 54.8 (CH_2), 43.2, 29.8, 29.6, 25.0; HRMS: found 254.1671, calc for $C_{18}H_{22}O$ 254.1670.

Reduction of *exo*-chloride 14a

454 mg (2.08 mmol) of *exo*-chloride **14a** and HO^{t}Bu (*tert*-buthanol) (3 mL) were dissolved in dry ether (20 mL). Excess metallic Na (2.0 g, 83 mmol), in small pieces, was added over a period of 10 min. After stirring at room temperature for 6 days, unreacted Na and solid KO^{t}Bu were removed by filtration and washed with ether (100 mL). The solution was poured into water (100 mL) and the mixture formed was shaken. The organic layer was separated, and the water layer was extracted twice with ether (2×30 mL). The combined organic layer was washed with water (20 mL), dried over $CaCl_2$ and then the solvent was evaporated. The product **19** was obtained as a pale yellow liquid (295 mg, 77%).

***anti*-12-Vinyltricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene (19).** δ_H (200 MHz, $CDCl_3$) 7.34–7.13 (m, aromatic, 4H), 6.25 (ddd, J=17.3, 10.4, 7.3 Hz, olefinic, 1H), 6.05 (m, olefinic, 1H), 5.37 (m, olefinic, 1H), 5.33 (dd, J=17.3, 2.2 Hz, olefinic, 1H), 5.21 (dd, J=10.4, 2.2 Hz, olefinic, 1H), 3.23–3.11 (m, bridge and bridgehead, 3H), 2.51 (dm, J=18.7 Hz, A part of AB-system, methylenic, 1H), 2.03 (dm, J=18.7 Hz, B part of AB-system, methylenic, 1H); δ_C (50 MHz, $CDCl_3$) 154.2 (C), 148.6 (C), 140.1 (CH), 132.6 (CH), 128.0 (2CH), 126.6 (CH), 125.4 (CH), 122.3 (CH), 118.4 (CH_2), 54.6 (CH), 46.9 (CH), 46.3 (CH), 30.6 (CH_2); ν_{max} ($CHCl_3$) 3105, 2978, 2842, 1622, 1448, 1388, 1193, 1154, 1006, 916, 741, 691 cm^{-1}; m/z 183/182/181/177 (26/71/37/27), 167/165 (78/64), 153/152 (59/43), 141 (92), 128 (100), 115 (65), 63 (30); Anal. Calcd For $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.35; H, 7.69.

Reduction of *endo*-chloride 15a

203 mg (0.93 mmol) *endo*-chloride **15a** and HO^{t}Bu (4 mL) was dissolved in dry ether (20 mL). Excess metallic Na (1.2 g, 52 mmol) of small pieces were added during 10 min and the mixture was stirred for 8 day. The other parts of the reaction were studied such as that of *exo*-chloride **14a** and the product **19** was obtained as pale yellow liquid (110 mg, 64%).

Reduction of chloride 18

174 mg (0.8 mmol) chloride **18** and HO^{t}Bu (3 mL) was dissolved in dry ether (20 mL). Excess metallic Na (1.5 g, 62.5 mmol), in small pieces, was added over a period of 10 min, and the mixture was stirred for 4 days. The other parts of the reaction were studied in the same manner as the *exo*-chloride **14a**, and the product **19** was obtained as a pale yellow liquid (90 mg, 61%)

Reduction of chloride 13b

560 mg (2.56 mmol) of chloride **13b** and HO^{t}Bu (5 mL) were dissolved in dry ether (20 mL). Excess metallic Na (2.0 g, 83 mmol), in small pieces, was added over a period of 10 min and the mixture was stirred for 4 days. The other parts of the reaction were studied in the same manner as the *exo*-chloride **14a**, and the product **23** was obtained as a liquid (280 mg, 59%).

***anti*, *exo*-Tetracyclo[6.3.2.0^{2,7}.0^{9,11}]tetradeca-2,4,6,12-tetraene-10-ylmethane (23).** δ_H (200 MHz, $CDCl_3$) 7.28–7.23 (AA′ part of AA′BB′-system, aromatic, 2H), 7.12–7.10 (BB′ part of AA′BB′-system, aromatic, 2H), 6.20 (m, olefinic, 2H), 4.05 (m, bridgehead, 2H), 1.19 (m, cyclopropane, 1H), 1.06 (d, J=2.8 Hz, methyl, 3H), 1.05 (m,

cyclopropane, 2H); δ_C (50 MHz, $CDCl_3$) 149.3 (C), 133.8 (CH), 126.5 (CH), 124.9 (CH), 43.5 (CH), 27.9 (CH), 23.7, 18.6; ν_{max} (liquid film) 3080, 3029, 2978, 2927, 2902, 2876, 1625, 1472, 1370, 1242, 1165, 1114, 1063 cm^{-1}; Anal. Calcd For $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.31; H, 7.76.

Reaction of chloride 13b in NaOMe/MeOH

500 mg (20.8 mmol) of metallic Na was dissolved in dry methanol (50 mL), and then chloride **13b** (144 mg, 0.66 mmol) and $AgNO_3$ (500 mg, 2.94 mmol) were added. The mixture was refluxed for 6 days and then cooled to room temperature. The mixture was filtered and the solvent was evaporated. The residue was submitted to PLC with EtOAc/hexane (1:9). *exo*-methoxide **14b** (70 mg, 50%, liquid), *endo*-methoxide **15b** (27 mg, 19%, liquid) and **13c** (33 mg, 23%, liquid) were isolated as pure.

***anti*, *exo*-11-Methoxy-12-vinyltricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-triene (14b).** δ_H (200 MHz, $CDCl_3$) 7.38–7.15 (m, aromatic, 4H), 6.48 (ddd, *J*=8.5, 10.3, 17.2, Hz, olefinic, 1H), 6.22 (bdd, *J*=6.5, 9.6, Hz, olefinic, 1H), 5.56 (dm, *J*=9.6, Hz, olefinic, 1H), 5.19 (dd, *J*=17.2, 1.6 Hz, olefinic, trans, terminal, 1H), 5.10 (dd, *J*=10.3, 1.6 Hz, olefinic, cis, terminal, 1H), 3.50 (m, C*H*–OMe, 1H), 3.46 (s, OMe, 3H), 3.39 (m, bridgehead C*H*CH–OMe, 1H), 3.27 (m, 1H), 3.19 (m, 1H); δ_C (50 MHz, $CDCl_3$) 154.5 (C), 146.3 (C), 140.7 (CH), 135.7 (CH), 128.2 (CH), 128.0 (CH), 126.4 (CH), 126.3 (CH), 123.1 (CH), 117.3 (CH_2), 79.7 (CH), 58.7 (OMe), 55.5 (CH), 50.0 (CH), 48.2 (CH); ν_{max} ($CHCl_3$) 3105, 2970, 2942, 2836, 1747, 1613, 1439, 1439, 1388, 1339, 1293, 1165, 1089, 1055, 991, 904, 804, 744, 724 cm^{-1}; HRMS: found 212.1201, calc for $C_{15}H_{16}O$ 212.1201.

***anti*, *endo*-11-Methoxy-12-vinyltricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-triene (15b).** δ_H (200 MHz, $CDCl_3$) 7.30–7.07 (m, aromatic, 4H), 6.24–6.06 (m, olefinic, 2H), 5.38 (bd, *J*=10.6 Hz, =C*H*CHOMe, 1H), 5.29 (bd, *J*=17.2 Hz, olefinic, terminal, trans, 1H), 5.16 (bd, *J*=11.3 Hz, olefinic, terminal, cis, 1H), 3.94 (m, C*H*-OMe, 1H), 3.56 (m, 1H), 3.45 (s, OMe, 3H), 3.37–3.30 (m, bridgehead, 1H), 3.16 (m, 1H); δ_C (50 MHz, $CDCl_3$) 154.4 (C), 144.1 (C), 139.0, 134.7, 128.3 (2CH), 128.0, 126.3, 122.5, 119.3, 76.8, 60.3, 58.2, 50.9, 46.8; ν_{max} ($CHCl_3$) 3105, 2964, 2836, 1747, 1613, 1433, 1382, 1333, 1199, 1082, 988, 924, 794, 742, 690 cm^{-1}; Anal. Calcd For $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.71; H, 7.68.

***anti*, *exo*-Tetracyclo[6.3.2.0^{2,7}.0^{9,11}]tetradeca-2,4,6,12-tetraene-10-yl-metoxymethane (13c).** δ_H (200 MHz, $CDCl_3$) 7.22–7.16 (AA′ part of AA′BB′-system, aromatic, 2H), 7.08–7.02 (BB′ part of AA′BB′-system, aromatic, 2H), 6.20 (m, olefinic, 2H), 4.03 (m, bridgehead, 2H), 3.32 (s, OMe, 3H), 3.23 (d, *J*=7.0 Hz, CH_2OMe, 2H), 1.55–1.45 (m, cyclopropane, 1H), 1.22 (m, cyclopropane, 2H); δ_C (50 MHz, $CDCl_3$) 149.0 (C), 133.9 (CH), 126.6 (CH), 125.0 (CH), 75.9 (CH_2), 60.5 (OMe), 43.1 (CH), 28.8 (CH), 24.8 (CH); ν_{max} ($CHCl_3$) 3020, 2890, 2800, 1774, 1434, 1383, 1334, 1242, 1122, 1086, 1052, 928, 772, 754, 730 cm^{-1}; HRMS: found 212.1211, calc for $C_{15}H_{16}O$ 212.1201.

Catalytic hydrogenation of 19

Into a 50 mL, two necked, round-bottomed flask, provided with a spinbar, were placed 15 mg of Pd/C (10%) catalyst and 0.8 mmol (147 mg) of **19** in ethylacetate (25 mL). One of the necks was attached to a hydrogen manifold with a three-way stopcock and the other neck was capped with a rubber septum, degassed and flushed with hydrogen gas, while stirring magnetically. After stirring for 10 h the solution was decanted to separate it from the catalyst, and the solvent evaporated. The residue was submitted to PLC with hexane. Compounds **20** (94 mg, 63% as yellow liquid) and **21** (35 mg, 24% as yellow liquid) were isolated as pure.

***anti*-12-Etyltricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene (20).** δ_H (200 MHz, $CDCl_3$) 7.30–7.11 (m, aromatic, 4H), 5.36 (m, olefinic, 1H), 5.33 (dm, *J*=9.5 Hz, olefinic, 1H), 3.12 (dd, *J*=6.5, 3.9 Hz, =CHC*H*, 1H), 3.01 (dd, *J*=4.4, 3.7 Hz, =CHCH_2CH,1H), 2.38 (dm, *J*=18.3 Hz, A part of AB-system, methylenic, 1H), 2.35 (m, bridge, 1H), 1.94 (dm, *J*=18.3 Hz, B part of AB-system, methylenic, 1H), 1.63 (m, CH_2CH$_3$, 2H), 1.02 (t, *J*=7.39 Hz, CH$_2$CH_3, 3H); δ_C (50 MHz, $CDCl_3$) 155.1 (C), 148.4 (C), 132.2 (CH), 127.8 (2CH), 126.6 (CH), 125.4 (CH), 122.3 (CH), 52.9 (CH), 45.3 (CH), 43.9 (CH), 30.1 (CH), 23.0 (CH_2), 14.5 (CH_3); ν_{max} ($CHCl_3$) 3072, 2958, 2806, 1476, 1423, 1372, 1180, 1030, 757, 735, 691 cm^{-1}; Anal. Calcd For $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.18; H, 8.75.

***anti*-12-Etyltricyclo[6.3.1.0^{2,7}]dodeca-2,4,6-trienene (21).** δ_H (200 MHz, $CDCl_3$) 7.16 (bs, aromatic, 4H), 2.93 (m, bridgehead, 2H), 2.15–2.07 (m, bridge, 1H), 1.86–1.66 (m, 2H), 1.67 (q, *J*=7.4 Hz, CH_2CH$_3$, 2H), 1.41–1.26 (m, 3H), 1.00 (t, *J*=7.4 Hz, CH$_2$CH_3, 3H), 0.94–0.77 (m, 1H); δ_C (50 MHz, $CDCl_3$) 149.7 (C), 128.1 (CH), 124.3 (CH), 78.4 (CH), 53.5 (CH), 44.6 (CH_2), 24.4 (CH_2), 19.5 (CH_2), 13.9 (CH_3); ν_{max} ($CHCl_3$) 3105, 2958, 2831, 1761, 1442, 1390, 1341, 1200, 1161, 1123, 1051, 1019, 958, 785, 747, 679 cm^{-1}; Anal. Calcd For $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.34; H, 9.70.

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