The Barrier to Rotation about the Double Bond in Methylenecyclopropane

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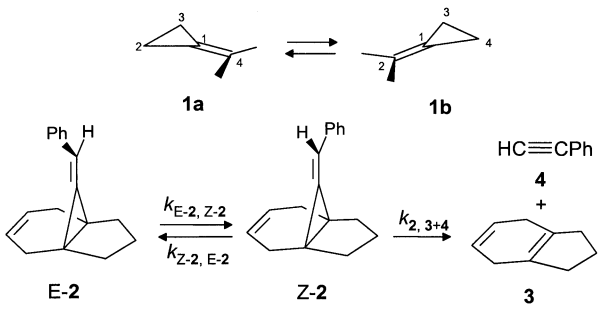
Activation parameters have been determined in the gas phase for the geometrical isomerization of the double bonds in two phenyl-substituted methylenecyclopropanes (**2** and **8**). Comparison with the analogous values for three sterically non-restricted styrene derivatives (**15**, **16** and **17**) shows that the enthalpies of activation for the methylenecyclopropanes are lower by 3.7 kcal mol^{-1}. This value, which is an upper limit to the amount of strain energy released by pyramidalization of the ring carbon atom in the orthogonal diradical transition state when undergoing geometrical isomerization, is considerably smaller than the value of 12–14 kcal mol^{-1} by which the strain energy of methylenecyclopropane is larger relative to that of cyclopropane. Our kinetics experiments thus show that the angle strain, associated with incorporating a trigonal carbon atom into the three-membered ring, is not responsible for the majority of the additional strain energy of methylenecyclopropane, relative to that of cyclopropane.

Due to their configurational flexibility, radicals in strained rings should adopt nonplanar geometries. The experimental verification of this hypothesis has been sought mainly by the analysis of the coupling constants of the ESR spectra of these radicals.[1]

The energy that is released by pyramidalization of a strained radical center should be assessable from the rotational barrier about a double bond to that center. In the transition state for geometrical isomerization, pyramidalization of one or both of the trigonal carbon atoms of the double bond can reduce the strain associated with the planarity of these carbon atoms in the reactant. Carbon-atom pyramidalization in the transition state should thus lower the rotational barrier, compared to the value expected for a transition state in which the trigonal carbon atoms are planar. The rotational barrier in the latter type of alkene can be calculated with a high degree of reliability by force-field methods.[2]

The barrier to rotation about the exocyclic methylene group in methylenecyclopropane (**1**) should be substantially reduced by pyramidalization of the ring carbon atom in the transition state. Wiberg and Fenoglio[3] have shown experimentally that the heat of formation of the cyclopropane ring is raised by 12−14 kcal mol^{-1} by the introduction of each trigonal carbon atom, and this increase was attributed to the additional angle strain caused by an sp^2-hybridized center. If this additional strain energy is removed by pyramidalization when an sp^2-carbon atom becomes a radical center, the enthalpy of activation for rotation about the double bond in methylenecyclopropane (**1**) should have the unusually low value of $\Delta H^{\neq} = 65.9$[4] $- 13 = 53$ kcal mol^{-1}. An experimental test of this prediction is the subject of this paper.

Scheme 1



Due to the much faster degenerate rearrangement **1a** ⇌ **1b**,[5] the barrier to rotation about the double bond in methylenecyclopropane (**1**) cannot be measured in the unsubstituted molecule. A suitable derivative of **1**, in which this reaction cannot take place, is propellane **2**. The introduction of the phenyl group allows the racemization of **2** to occur at temperatures where fragmentation to dihydroindane **3** and phenylacetylene (**4**) is of only minor importance.[6]

The synthesis of **2** was achieved by the Seebach route[7] starting from the propellane **5**.[8] Separation of the enantiomers was performed by HPL chromatography, using a triacetylcellulose column, which yielded E- and Z-**2** with 100% ee.

Thermolysis of **2** in the gas phase at temperatures > 380°C gives rise to racemization, accompanied by a slower fragmentation of **2** to **3** and **4**. Under the reaction conditions, **3** aromatizes to indane. The rates of racemization and fragmentation were measured at 8 and 6 temperatures (in the range 344−430°C), respectively. The ratio of the enantiomers was analysed by HPL chromatography. From the

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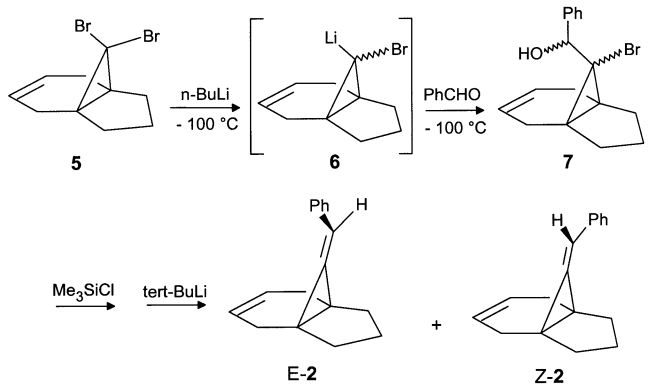
Scheme 2



first-order rate constants (Tables 2 and 3) the corresponding activation parameters in Table 1 have been derived.

Table 1. Activation parameters for reactions of **2** and **8**

	T_m[b]	E_A[c]	log A	$\Delta H^{\neq}$[c]	$\Delta S^{\neq}$[d]
$k_{E\text{-}2,Z\text{-}2}$	375	51.1±1.1	13.03±0.40	49.8±0.4	−2.5±1.8
$k_{2,3+4}$	406	54.8±0.9	13.28±0.30	53.5±0.9	−1.4±1.4
$k_{Z\text{-}8,E\text{-}8}$	394	50.6±1.4	12.91±0.46	49.3±1.4	−3.1±2.1
$k_{E\text{-}8,Z\text{-}8}$	394	50.6±1.4	12.87±0.47	49.2±1.4	−3.1±2.2
$k_{8,11+4}$	394	54.7±1.9	13.28±0.62	53.4±1.9	−1.4±2.8

[a]Error limits are based on a 95-% confidence level. [b]°C. − [c] kcal mol^{-1}. − [d] cal K^{-1} mol^{-1}.

Table 2. Rate constants for the interconversion E-**2** ⇌ Z-**2**

T [°C]	344.2	349.7	358.9	369.7	379.3	389.9	399.2	409.3
$k_{E\text{-}2,Z\text{-}2}$ 10^5 [s^{-1}]	0.866	1.269	2.307	4.339	7.921	14.77	25.72	47.91

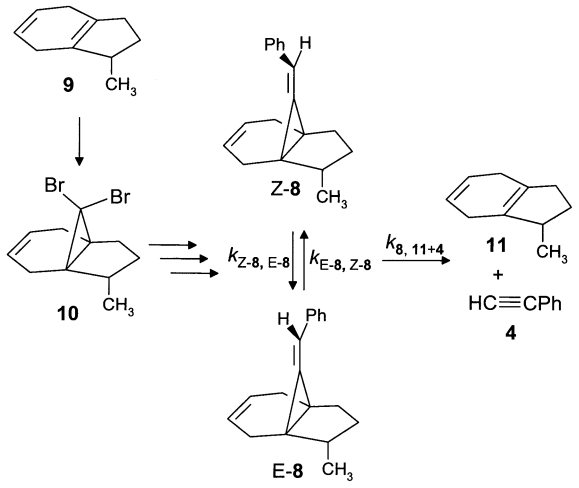
Table 3. Rate constants for the rearrangement **2** → **3** + **4**

T [°C]	379.9	389.5	399.5	414.3	425.0	429.2
$k_{2,3+4}$ 10^5 [s^{-1}]	0.855	1.589	2.967	7.309	12.83	16.91

In order to verify the results obtained with **2**, the geometrical isomerization of the methyl derivatives Z-**8** ⇌ E-**8** was measured. The synthesis of **8** was achieved in analogy to that of **2**, using the dihydromethylindane **9**[9] as starting material. Separation of the isomers was performed by HPL chromatography.

Gas-phase thermolysis of E-**8** and Z-**8** at temperatures > 370°C gives rise to the interconversion of these isomers and to a slower fragmentation, yielding compounds **4** and **11**. The latter also aromatizes giving 1-methylindane. The rates of these reactions were measured at 6 temperatures (in the range 370−420°C). From the first-order rate constants (Tables 4 and 5) the activation parameters in Table 1 were

Scheme 3



derived. They agree well with the values obtained from the thermolysis of **2**.

Table 4. Rate constants for the interconversion E-**8** ⇌ Z-**8**

T [°C]	369.6	379.8	390.3	399.8	410.3	420.4
$k_{Z\text{-}8,E\text{-}8}$ 10^5 [s^{-1}]	4.932	9.173	17.26	29.40	52.13	89.78
$k_{E\text{-}8,Z\text{-}8}$ 10^5 [s^{-1}]	4.783	8.885	17.16	28.26	50.46	87.09

Table 5. Rate constants for the rearrangement **8** → **11** + **4**

T [°C]	369.7	379.7	389.8	400.0	409.6	420.1
$k_{8,11+4}$ 10^5 [s^{-1}]	0.472	0.908	1.693	3.356	5.695	10.58

At this point some attention has to be given to the mechanism of the geometrical interconversion of the stereoisomers of compounds **2** and **8**. In order to derive the relief of angle strain in the diradical **13** from the barrier of activation for the geometrical interconversions, it has to be ensured that these geometrical interconversions occur via the transition state **13** and not by a vinylic ring-opening reaction. For the racemization of the propellane **12,** Meier determined the activation parameters quoted in Table 6.[6] If we accept the activation enthalpies for the isomerization of **2** and **8** as the lower limit of the barrier to rotation about a methylencyclopropane-type double bond, then the racemization of **12** cannot take place by a double-bond rotation mechanism. Such a reaction should have an activation enthalpy of nearly 60 kcal mol^{-1}, because the stabilizing effect of the phenyl group, which lowers the barrier to rotation about a double bond by 10 kcal mol^{-1},[2] is missing in propellane **12**. Therefore, the only possible reaction mechanism for the racemization of **12** is a vinylic methylenecyclopropane ring-opening mechanism. With this knowledge of the activation enthalpy for the competitive ring-opening reaction, the activation enthalpies of the geometrical interconversion of **2** and **8**, which are lower by 3.7 and 4.2 kcal mol^{-1} respectively, can unambiguously be assigned to the

double-bond rotation mechanism. The very good agreement between the activation enthalpy of the racemization of **12** and the activation enthalpy of the fragmentation reactions of **2** and **8** furthermore indicates, that the latter occur by a vinylic ring-opening reaction as the rate-determining step.

Scheme 4

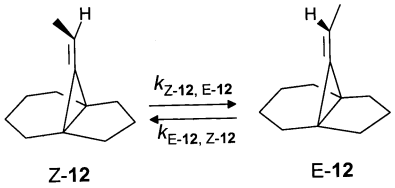
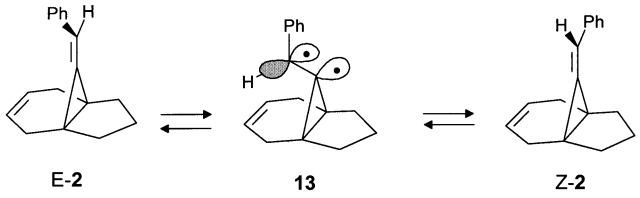


Table 6. Activation parameters for the racemization of **12**[6]

	T_m[a]	E_A[b]	log A	$\Delta H^{\neq}$[b]	$\Delta S^{\neq}$[c]
$k_{E\text{-}12,Z\text{-}12}$	400	54.8±0.5	13.11	53.5±0.5	−2.1

[a] °C. − [b] kcal mol^{-1}. − [c] cal K^{-1} mol^{-1}.

Scheme 5



Having furnished proof of the double-bond rotation mechanism for the isomerization of propellanes **2** and **8**, the next step is to determine the relief of angle strain during the isomerization of **2** and **8** by comparison with the barriers to rotation about the double bond of unstrained styrene derivatives. The difference between the mean of the enthalpies of activation for rotation about the double bonds in **2** and **8** (49.4 kcal mol^{-1}; Table 1) and the mean of the enthalpies of activation for the geometrical interconversion of the styrene derivatives Z-**15**, E-**16** and E-**17** (51.8 kcal mol^{-1}; Table 7)[2] gives a value of only 2.4 kcal mol^{-1} for the relief of angle strain. However, these 2.4 kcal mol^{-1} are only a minimum value for the stabilization of the orthogonal diradical **13**, because the different steric contributions in the propellanes **2** and **8** and in the reference molecules **15**−**17** have to be considered. In contrast to the nonplanar *cis*-substituted styrene derivatives **15**−**17**,[2] (phenylmethylene)cyclopropane (**14**), which serves as a reference molecule for the structure of **2** and **8**, is planar[10] and therefore does not show any significant steric interaction between the phenyl group and the vinylic cyclopropane bonds. As a result, 2.4 kcal mol^{-1} is only a minimum value for the stabilization of the orthogonal diradical **13**.

According to force-field calculations,[2] the steric contribution of the methyl groups in the styrene derivatives **15**−**17** lowers the rotational enthalpy by 1−2 kcal mol^{-1}. This value agrees well with the difference between the E → Z and Z → E activation enthalpies for the stereoisomers

Scheme 6

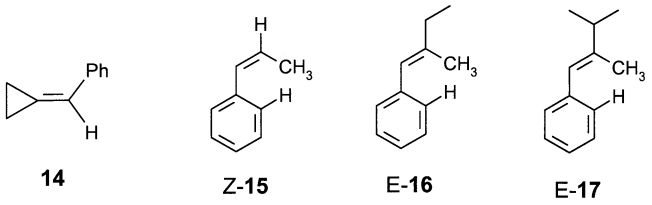


Table 7. Rotational enthalpies ($\Delta H^{\neq}$) [kcal mol^{-1}] of styrene derivatives[2]

	15	16	17
Z → E	51.9±0.4	52.0±0.5	51.3±2.0
E → Z	53.2±0.9	51.9±0.4	51.8±1.6

of **15** ($\Delta\Delta H^{\neq}$ = 1.3 kcal mol^{-1}). After correction for this difference, a stabilization energy for the diradical **13** of ΔE = 3.7 kcal mol^{-1} is obtained. This stabilization energy comprises the energy released by pyramidalization of the cyclopropyl radical, and the stabilizing interaction of the benzylic radical with the bent bonds of the cyclopropane ring.[11] Thus, instead of the expected strain release of 12−14 kcal mol^{-1} in **13**, an experimental value of < 3.7 kcal mol^{-1} is observed.

As shown in the theoretical analyses by Borden and Johnson,[11] this discrepancy between the results of our kinetics experiments and the thermochemistry measured by Wiberg and Fenoglio[3] comes from assuming that all of the "extra" strain of 12−14 kcal mol^{-1} in methylenecyclopropane (**1**) is due to the additional angle strain, introduced by incorporating a trigonal carbon atom in the three-membered ring. In agreement with the quantum-chemical calculations of Borden and Johnson, pyramidalization in the transition state for the geometrical isomerization of **2** and **8** lowers the strain by less than 4 kcal mol^{-1}. The dominant part (9−10 kcal mol^{-1}) of the "extra" heat of formation of methylenecyclopropane (**1**) is, according to Borden and Johnson,[11] connected with the unusual strength of the C−H bonds in cyclopropane, since these C−H bonds are lost when a trigonal carbon atom is introduced into the three-membered ring.

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Experimental Section

1. *Kinetic Measurements*

The rate constants, listed in Tables 2−5 have been measured with the techniques and apparatus described in the literature.[12] In general, less than 1 ml of a solution comprising nearly 1% of a pure isomer or a pure enantiomer and nearly 0.5% of an inert internal standard in hexane was placed into an evacuated 20-l reaction flask by a syringe. During the thermolysis reaction the variation in temperature is less than ±0.1 °C. After certain periods, samples were taken from the flask and analysed by an attached GL chromatograph. Both rate constants and activation parameters were calculated by simulating the thermolysis reaction, using the simplex

method[13] for the best-fit analysis. For simulation of the geometrical interconversion reactions, the percent concentration of the stereoisomers, referred to the sum of both of the stereoisomers, were used. Simulation of the fragmentation reaction was performed using the percent concentration of propellane, referred to *n*-tetradecane as the internal standard. The uncertainty limits quoted in Table 1 are based on a 95-% confidence level and have been calculated for the data obtained by simulation according to the method of Nelder.[14]

Racemization of 10-Benzylidenetricyclo[4.3.1.0^{1,6}]dec-3-ene (**2**): The rate constants for the racemization of **2** have been measured by thermolysing 500-ml portions of a 0.5% solution of **2** in hexane using the apparatus described in the literature.[12] After a certain reaction time the material was condensed for 20 s into a 50-ml flask, which was attached to the reaction flask by a glass tube and a Quickfit connector. The flask was cooled to −196°C and the vacuum was maintained at 10^{-2} Torr. By this method 150−200 ml of a 0.01% solution was recovered. Analysis was carried out by HPLC on CHIRACEL OD−H [5 μ, (250 × 4.6) mm, with precolumn 10 μ, (50 × 4.6) mm, Baker] with hexane (0.5 ml min^{-1}, 5°C), R_t = 18.96 and 22.66 min.

Fragmentation of 10-Benzylidenetricyclo[4.3.1.0^{1,6}]dec-3-ene (**2**): Analysis was performed by GLC: Column OV1 (50 m, diameter 0.2 mm, 190°C, 2.0 bar N_2); R_t(**4**) = 5.46 min; R_t(indane) = 6.09 min; R_t(**2**) = 23.91 min. Fragmentation products were identified by comparison with the retention times of authentic samples, and by GLC-MS analysis of the thermolysis mixture, respectively. − **4**: *m/z* (%): 102 (100) [M$^+$], 91 (3), 76 (31), 63 (5).; indane: *m/z* (%): 118 (63) [M$^+$], 117 (100), 115 (31), 103 (4), 91 (13), 89 (6).

Thermolysis of 10-Benzylidene-endo-7-methyltricyclo[4.3.1.0^{1,6}]-dec-3-ene (**8**): Analysis was performed by GLC: Column QF1 (60 m, diameter 0.2 mm, 170°C, 2.0 bar N_2); R_t(**4**) = 4.76 min; R_t(1-methylindane) = 5.52 min; R_t(Z-**8**) = 26.87 min; R_t(E-**8**) = 27.37 min. Fragmentation products were identified both by comparison with the retention times of authentic samples and by GLC-MS analysis of the thermolysis mixture. − **4**: *m/z* (%): 102 (100) [M$^+$], 91 (4), 76 (30), 63 (7); 1-methylindane: *m/z* (%): 132 (24) [M$^+$], 117 (100), 115 (29), 102 (3), 91 (14), 77 (5). − Thermolysis of a sample of 1-methyl-4,7-dihydroindane (**9**) at 380°C for 4000 s led to complete rearrangement to 1-methylindane.

2. *Preparations*

Equipment: NMR: Bruker AM-400, AM-200. − GLC MS: Hewlett Packard 5890 A Series II gas chromatograph (column OV1, 12.5 m, diameter 0.33 mm) and mass-selective detector Hewlett Packard 5979 Serie MSD. − IR: Perkin-Elmer 681. − Analytical GLC: Intersmat IGC 120 F8, Hewlett-Packard 5890 Serie II; nitrogen was used as carrier gas. − Integrators: Hewlett Packard 3390 A, 3395. − Analytical HPLC: Spectra-Physics SP5750 organizer, SP 8700 solvent delivery system, Shimadzu SPD-6A spectrophotometer . − Preparative HPLC: Shimadzu LC-8A, Waters Associates chromatography pump, Altex analytical UV detector + preparative analytical optical unit, Knauer UV/VIS filter photometer.

General: All preparations were performed under argon and with oven-dried glassware. Silica-gel chromatography was performed on silica gel Si 60 (60−250μ, Macherey and Nagel).

(10-Bromotricyclo[4.3.1.0^{1,6}]dec-3-en-10-yl)phenylmethanol (**7**): A stirred solution of 2.0 g (6.8 mmol) of 10,10-dibromotricyclo[4.3-.1.0^{1,6}]dec-3-ene (**5**)[8] in 14 ml of dried THF was cooled to −110°C and 4.25 ml (6.8 mmol) of *n*-BuLi (1.6 M in hexane) was added dropwise within 10 min. During the addition the temp. did not rise above −95°C. After 5 min of stirring, 712 mg (690 ml, 6.8 mmol) freshly distilled benzaldehyde was added, while the temp. was kept below −100°C. After 3 h of stirring at −100 to −90°C, the solution was warmed to −45°C within 1.5 h, 40 ml of water was added, the THF layer was separated, and the aqueous layer was extracted with pentane (3 × 25 ml). The combined organic layers were washed with brine and dried with $MgSO_4$. Purification of the diastereomeric mixture (analytical GLC, column OV1, 25 m, diameter 0.33 mm, 200°C, R_t = 13.2 and 13.4 min, ratio 2.5:12.1) was achieved by silica-gel chromatography using hexane/diethyl ether (2:1), affording 1.7 g (5.3 mmol, 78%). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.8−2.6 (m, 11 H, CH_2 and OH), 4.51 und 4.54 [2 d, 1 H, *J* = 10.5 Hz, CH (benzylic)], 5.48−5.46, 5.63, 5.65−5.73 [m, br. s, m, 2 H, CH (olefinic)], 7.25−7.47 (m, 5 H, CH). − ^{13}C NMR (100.6 MHz, $CDCl_3$): main diastereomer: δ = 26.79, 30.02, 30.76, 36.77, 37.63 (CH_2), 33.73, 35.10 (C), 64.71 (C), 72.87 (CH, benzylic), 123.61, 124.36 (CH, olefinic), 126.17, 127.16, 127.23 (CH), 143.13 (C); 2nd diastereomer: δ = 26.10, 26.73, 26.99, 40.22, 40.56 (CH_2), 68.05 (C), 72.65 (CH, benzylic), 124.20, 124.89 (CH, olefinic), 127.17, 127.89 (CH), the signals of 3 quarternary carbon atoms and of one CH group could not be determined, presumably due to signal overlap or weak intensity. − IR (neat): $\tilde{\nu}$ = 3450 (m), 3080 (w), 3060 (w), 3020 (m), 2950 (s), 2920 (s), 2890 (m), 2870 (m), 1490 (m), 1450 (m), 1425 (m), 1380 (m), 1230 (w), 1195 (w), 1185 (w), 1145 (w), 1095 (m), 1070 (m), 1050 (m), 1030 (m) 1010 (m), 745 (m) 700 (s) cm^{-1}. − GLC MS (70 eV); *m/z* (%): 318 (1) [M$^+$], 302 (3), 300 (3), 266 (7), 264 (7), 243 (21), 241 (24), 239 (21), 221 (24), 211 (8), 198 (15), 197 (15), 185 (14), 184 (14), 179 (14), 178 (12), 141 (18), 133 (17), 125 (19), 117 (22), 115 (27), 107 (18), 105 (100), 91 (97), 79 (44), 77 (81), 65 (18), 51 (24), 41 (20), 39 (24).

(10-Bromotricyclo[4.3.1.0^{1,6}]dec-3-en-10-yl)phenylmethyl Trimethylsilyl Ether (**18**): 379 mg (490 ml, 2.35 mmol) of hexamethyldisilazane and 511 mg (594 ml, 4.7 mmol) of chlorotrimethylsilane were added dropwise to a vigorously stirred solution of 1.5 g (4.7 mmol) of **7** in 14 ml of dried pyridine. After additional 2 h of stirring, the reaction mixture was poured into 10 ml of ice/water and extracted with pentane (3 × 25 ml). The combined pentane layers were washed with brine and dried with $MgSO_4$. The solvent was distilled off and the crude residue was chromatographed on silica gel using hexane/diethyl ether (15:1), yielding 1.53 g of a diastereomeric mixture (3.91 mmol, 83%).− ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05, 0.22 (2 s, 9 H, $SiCH_3$), 1.55−2.90 (m, 10 H, CH_2), 4.75, 4.90 [2 s, 1 H, CH (benzylic)], 5.68, 5.6−5.95 [br. s and m, 2 H, CH (olefinic)], 7.25−7.60 (m, 5 H, CH). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 1.31, 1.39 ($SiCH_3$), 26.89, 26.99, 27.84, 27.96, 30.70, 31.29, 34.35, 34.54, 35.49, 35.61, 37.17, 38.39, 41.43, 41.58 (CH_2 and C), 63.60, 66.18 (CBr), 74.54, 74.80 (CO), 124.46, 124.81, 125.05 (C, olefinic), 126.38, 127.36, 127.48, 127.81, 128.17, 129.02 (CH), 143.72, 144.23 (C). − IR (neat): $\tilde{\nu}$ = 3020 (w), 2950 (m), 2920 (m), 2900 (m), 1495 (w), 1450 (m), 1430 (w), 1260 (m), 1250 (s), 1090 (s), 1070 (m), 1030 (m), 910 (m), 890 (m), 865 (m), 840 (s) 750 (m), 700 (m) cm^{-1}. − GLC MS (70 eV); *m/z* (%): 302 (17) [M$^+$ − Me_3SiOH], 300 (18) [M$^+$ − Me_3SiOH], 221 (36), 203 (8), 193 (14), 191 (17), 179 (32), 178 (34), 167 (16), 165 (33), 151 (14), 143 (19), 141 (23), 129 (32), 128 (32), 117 (44), 116 (44), 105 (24), 102 (16), 91 (100), 89 (19), 77 (25), 65 (14), 51 (15), 41 (13), 39 (20).

10-Benzylidenetricyclo[4.3.1.0^{1,6}]dec-3-ene (**2**): A solution of 1.23 g (3.14 mol) of **18** in 30 ml of dry THF/pentane (1:1) was cooled to −110°C (ethanol/liquid nitrogen cooling bath). 6.15 ml (9.84 mol) of *t*BuLi (1.6 M in pentane) was added slowly while the temp. was not allowed to raise above −100°C. After this, the reaction mixture was warmed to −25°C within a period of 4 h and then hydrolysed with water (80 ml). The organic layer was separated and

the aqueous layer was extracted with pentane (3 × 25 ml). The combined organic layers were washed with brine (10 ml) and dried with $MgSO_4$. After evaporation of the solvent, silica-gel chromatography of the residue using hexane afforded 690 mg (3.1 mmol, 98%) of **2**. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17−1.30 (m, 1 H, CH_2), 1.55−1.65 (m, 1 H, CH_2), 1.72−1.83 (2 q, 2 H, J = 11.4 Hz, CH_2), 2.03−2.10 (dd, 1 H, J = 7.5/12.0 Hz, CH_2), 2.18−2.31 (m, 3 H, CH_2), 2.52−2.75 (m, 2 H, CH_2), 5.41−5.51 [m, 2 H, CH (olefinic)], 6.68 [s, 1 H, CH (benzylic)], 7.12−7.19 (m, 1 H, CH), 7.26−7.33 (m, 4 H, CH). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.00, 27.35, 28.34, 35.99, 36.29 (CH_2), 27.13, 29.25 (C), 114.13 (C, olefinic), 120.54 (C, benzylic), 123.66, 123.74 (CH, olefinic), 126.19, 126.82, 128.43 (CH), 137.92 (C). − IR (neat): $\tilde{\nu}$ = 3080 (w), 3060 (w), 3020 (m), 2960 (m), 2920 (m), 2900 (m), 2870 (m), 2850 (m), 2830 (m), 1600 (w), 1495 (m), 1455 (m), 1445 (m), 1435 (w), 1250 (w), 1200 (w), 1100 (w), 1075 (w), 1030 (w), 940 (w), 910 (m), 860 (w), 750 (m), 730 (m), 690 (s), 660 (m) cm^{-1}. − GLC MS (70 eV); *m/z* (%): 222 (80) [M^+], 207 (31), 194 (30), 193 (38), 181 (19), 180 (23), 179 (82), 178 (53), 167 (28), 165 (60), 152 (25), 141 (22), 131 (59), 129 (34), 128 (43), 104 (17), 92 (31), 91 (100), 89 (27), 79 (20), 77 (36), 65 (24), 63 (18), 51 (26), 41 (18), 39 (34). − Separation of the enantiomers was achieved by preparative HPLC using a triacetylcellulose column [15−25 μ, (250 × 20) mm, Merck] and ethanol/water (96:4; 4 ml/min) as the eluent (R_t = 28.0 and 43.0 min), yielding each enantiomer with 100% ee. Analysis of the enantiomeric mixtures was performed by HPLC using a CHIRACEL OD-H column [5 μ, (250 × 4.6) mm, with pre-column 10 μ (50 × 4.6) mm] and hexane (0.5 ml/min, 5°C); R_t = 18.96 and 22.66 min.

10,10-Dibromo-endo-7-methyltricyclo[4.3.1.0^{1,6}]dec-3-ene (**10**): 17.19 g (68.0 mmol) of bromoform was added within 2.5 h to a vigorously stirred suspension (−15°C) of 10.5 g (78.2 mmol) of 1-methyl-4,7-dihydroindane (**9**)[9] and 8.39 g (74.8 mmol) of KO*t*Bu in 15 ml of pentane. After 1 additional h of stirring at −15°C, the reaction mixture was poured into water (150 ml) and extracted with pentane (3 × 80 ml). The combined pentane layers were washed with brine (50 ml), dried ($MgSO_4$) and concentrated. The crude product was chromatographed on silica gel using hexane. The main fraction contained **10** with a purity of 75%. Minor components were an isomer of **10** (5%, identified by GLC MS), 4,7-dihydro-1-methylindane (10%) and a higher boiling compound (10%). The crude product was used in the next step without further purification. Yield: 4.60 g (15.5 mmol, 20%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.09 (d, 3 H, ^3J = 7.3 Hz, CH_3), 1.30−1.45 (m, 1 H), 1.90−2.65 (m, 8 H), 5.45−5.66 [m, 2 H, CH (olefinic)]. − GLC MS (70 eV); *m/z* (%): 308 (1) [M^+], 306 (2) [M^+], 304 (1) [M^+], 252 (3), 227 (12), 225 (12), 199 (6), 197 (6), 185 (8), 183 (8), 171 (19), 169 (14), 146 (37), 145 (77), 131 (29), 117 (32), 115 (36), 105 (31), 91 (100), 79 (28), 77 (67), 65 (30), 63 (29), 51 (42), 41 (29), 39 (56).

(10-Bromo-endo-7-methyltricyclo[4.3.1.0^{1,6}]dec-3-en-10-yl)-phenylmethanol (**19**): 5.51 ml (8.8 mmol) of *n*BuLi (1.6 M in hexane) was added dropwise within 5 min to a stirred solution of 3.0 g (75%, 7.35 mmol) of **10** in 18 ml of dried THF at −100°C. During the addition the temp. did not raise over −95°C. After 2 min, 935 mg (895 ml) of freshly distilled benzaldehyde was added by a syringe within 5 min. The solution was stirred for additional 2 h at −100°C and then warmed to −40°C within 2 h. The mixture was hydrolysed with water (70 ml), the THF layer was separated and the aqueous layer was extracted with pentane (3 × 30 ml). The combined organic layers were washed with brine (10 ml) and dried with $MgSO_4$. After evaporation of the solvent, the crude product was chromatographed on silica gel using hexane/diethyl ether (3:1). The main fraction contained **19** as a mixture of 2 diastereomers (analytical GLC, column OV1, 25m, diameter 0.33 mm, R_t = 22.89 and 23.24 min) with 80% purity. The main impurity (7%) was identified as unreacted benzaldehyde. The crude product [yield: 1.45 (3.48 mol, 40%)] was used in the next step without further purification. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.7−2.8 [m, 13 H, CH_2, CH, CH_3 and OH; within this signal: δ = 1.11, 1.14, 1.18 (2 d, 3 H, ^3J = 7.3/7.0 Hz, CH_3)], 4.59 [d, 1 H, ^3J = 11.3 Hz, CH (benzylic)], 5.55−5.73 [m, 2 H, CH (olefinic)], 7.20−7.60 (m, 5 H, CH). − GLC MS (70 eV); *m/z* (%): 318 (2) [$M^+ - H_2O$], 316 (1) [$M^+ - H_2O$], 280 (3), 278(3), 253 (6), 235 (10), 193 (8), 178 (10), 165 (10), 157 (10), 141 (11), 128 (14), 117 (16), 115 (26), 107 (22), 105 (83), 91 (100), 79 (52), 77 (84), 65 (19), 56 (18), 51 (27), 41 (23), 39 (23).

(10-Bromo-endo-7-methyltricyclo[4.3.1.0^{1,6}]dec-3-en-10-yl)-phenylmethyl Trimethylsilyl Ether (**20**): 350 mg (454 ml, 2.17 mol) of hexamethyldisilazane and 473 mg (550 ml, 4.35 mmol) of chlorotrimethylsilane were added slowly to a stirred solution of 1.45 g (80%, 3.48 mol) of **19** in 13 ml of dried pyridine. After 2 h of stirring, the mixture was poured into water (60 ml) and extracted with pentane (3 × 30 ml). The combined pentane layers were washed with brine (10 ml) and dried ($MgSO_4$). Purification of the crude product was achieved by silica-gel chromatography using hexane/diethyl ether (30:1), affording 1.17 g with 93% purity (2.68 mmol, 67%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.15, 0.17 (2 s, 9 H, $SiCH_3$), 0.80−2.70 (m, 12 H, CH_2, CH and CH_3; within this signal: δ = 1.10, 1.14, 1.18 (2 d, 3 H, ^3J = 7.5/7.2 Hz, CH_3)], 4.80, 4.81 [2 s, 1 H, CH (benzylic)], 5.50−5.71 [m, 2 H, CH (olefinic)], 7.20−7.45 (m, 5 H, CH). − GLC MS (70 eV); *m/z* (%): 391 (1) [$M^+ - CH_3$], 389 (1) [$M^+ - CH_3$], 330 (2), 325 (5), 271 (2), 235 (10), 193 (8), 179 (31), 165 (8), 152 (4), 141 (7), 132 (8), 128 (8), 117 (9), 115 (17), 105 (19), 91 (55), 79 (10), 77 (20), 75 (28), 73 (100), 45 (22).

Z/E-10-Benzylidene-endo-7-methyltricyclo[4.3.1.0^{1,6}]dec-3-ene (**8**): A solution of 1.17 g (93%, 2.68 mmol) of **20** in 30 ml of dried THF/pentane was cooled to −110°C (ethanol/liquid nitrogen cooling bath). 4.0 ml (6.4 mmol) of *t*BuLi (1.6 M in pentane) was added dropwise within 3 min while the temp. was kept below −98°C. The reaction mixture was then warmed to −25°C within 4.5 h and hydrolysed with 70 ml of water. The organic layer was separated and the aqueous layer extracted with pentane (3 × 30 ml). The combined organic layers were washed with brine (10 ml), dried with $MgSO_4$ and concentrated. Silica-gel chromatography using hexane yielded 480 mg of **8** with 92% purity (1.87 mmol, 69%). 100% purity was achieved by HPLC on LiChrospher [5 μ, (250 × 20) mm] using hexane (15 ml/min); R_t = 14.3 min. Separation of E-**8** and Z-**8** was carried out by HPLC using a CHIRACEL OD-H column [5 μ, (250 × 4.6) mm, with pre-column 10 μ, (50 × 4.6) mm] and hexane (0.5 ml/min, 5°C). By this manner 3 peaks were detected in a ratio of 2:1:1, which could be assigned as follows: R_t(E-**8** and Z-**8**, 1 enantiomer each) = 19.13 min; R_t(E-**8**, 2nd enantiomer) = 20.57 min; R_t(Z-**8**, 2nd enantiomer) = 23.98 min. Analysis of the isomeric mixtures was performed by GLC (column QF1, 60 m, diameter 0.2 mm, 180°C, 1.5 bar N_2): R_t(Z-**8**) = 29.87 min; R_t(E-**8**) = 30.97 min. The assignment of E-**8** and Z-**8** was based on the ^{1}H-NMR signal of the hydrogen atom at C-7, which is shifted 0.18 ppm downfield for the Z isomer (from ^{1}H-^{13}C-HMQC NMR spectra). − Z-**8**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (d; 3 H, ^3J = 7.0 Hz, CH_3), 1.24−1.31 (m, 1 H, CH_2), 1.43−1.55 (m,1 H, CH_2), 1.82−1.91 (dt, 1 H, J = 12.0 and 7.0 Hz, CH_2), 1.92−1.99 (dd, 1 H, J = 11.5 and 7.5 Hz, CH_2), 2.19−2.26 (m, 1 H, CH_2), 2.38−2.48 [m, 3 H, CH and CH_2, CH at 2.42 (from HMQC spectra)], 2.54−2.62 (m, 1 H, CH_2), 5.41−5.50 [m, 2 H, CH (olefinic)], 6.61 [s, 1 H, CH (benzylic)], 7.08−7.19 (m, 1 H, CH), 7.23−7.35 (m, 4 H, CH). − ^{13}C NMR (100.6 MHz, $CDCl_3$):

δ = 17.90 (CH_3), 22.79 (CH_2), 27.64 (C), 28.64 (CH_2), 29.70 (CH_2), 33.02 (C), 33.60 (CH_2), 38.59 (CH), 119.35 (CH, benzylic), 123.31, 124.36 (CH, olefinic), 126.11 (CH, *para*), 126.93, 128.43 (CH), 137.95, 141.00 (C). − E-**8**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (d, 3 H, ^3J = 7.0 Hz, CH_3), 1.23−1.30 (dd, 1 H, *J* = 7.0 and 13.04 Hz, CH_2), 1.44−1.55 (m, 1 H, CH_2), 1.85−1.94 (dt, 1 H, J = 7.0 and 12.0 Hz, CH_2), 2.08−2.16 (dd, *J* = 7.0 and 12.0 Hz, CH_2), 2.18−2.36 [m, 3 H, CH and CH_2, CH at 2.24 (from HMQC spectra)], 2.39−2.47 (m, 1 H, CH_2), 2.68−2.76 (m, 1 H, CH_2), 5.39−5.53 [m, 2 H, CH (olefinic)], 6.64 [s, 1 H, CH (benzylic)], 7.08−7.18 (m, 1 H, CH), 7.22−7.32 (m, 4 H, CH). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.33 (CH_3), 24.16, 27.85 (CH_2), 29.80 (C), 30.15 (CH_2), 30.88 (C), 33.20 (CH_2), 39.13 (CH), 119.51 (CH, benzylic), 123.43, 124.34 (CH, olefinic), 126.11 (CH, *para*), 126.85, 128.45 (CH), 138.03, 141.02 (C). − **8**: IR (neat): $\tilde{\nu}$ = 3080 (w), 3060 (w), 3020 (m), 2960 (s), 2890 (s), 2830 (m), 1650 (w), 1600 (m), 1490 (m), 1450 (m), 1435 (m), 1370 (w), 1330 (w), 1305 (w), 1215 (w), 1175 (w), 1070 (w), 1030 (w), 910 (m), 855 (m), 750 (m), 690 (s) cm^{-1}. − GLC MS (70 eV); *m/z* (%): 236 (20) [M^+], 221 (14), 207 (5), 194 (9), 193 (18), 179 (39), 178 (29), 167 (21), 165 (38), 152 (16), 145 (30), 141 (18), 129 (23), 128 (34), 117 (39), 115 (51), 105 (18), 102 (18), 91 (100), 89 (25), 79 (19), 77 (42), 65 (23), 63 (18), 51 (27), 41 (26), 39 (36).

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