Synthesis, Reactions, and Properties of 2,8-Didehydronoradamantane Derivatives

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2,8-Didehydronoradamantan-9-one (**2**) was readily prepared by oxa-di-π-methane photorearrangement of brend-4-en-2-one (**1**). Other new 9-substituted 2,8-didehydronoradamantanes have also been prepared from **2**, [i.e. 2,8-didehydronoradamantan-9-ol (**3**) and tosylhydrazone **4**] and the ring-opening reactions have been studied. In acidic media, 2,8-didehydronoradamantan-9-ol (**3**) rearranges to the corresponding 2-substituted brend-4-ene derivatives. Exclusive formation of *exo*-2-substituted brend-4-enes supports the formation of a bridged bicyclobutonium ion. However, treatment of ketone **2** with PCl_5 proceeds through a concerted mechanism by cleavage of the C-1–C-2 bond in **2** to give *exo*-2,5-dichlorotricyclo[4.2.1.0^{3,8}]non-4-ene (**6**). The tricyclo[4.2.1.0^{3,8}]nonane skeleton was also obtained by photochemically induced electron transfer reduction of **2** and reduction of **2** with Li/NH_3, as well as by reduction of tosylhydrazone **4** with both $NaBH_3CN$ and $BH_3 \times THF$. On the other hand, Wolff–Kishner reduction of **2** gave the nonrearranged product, 2,8-didehydronoradamantane (**10**).

It is well known that the cyclopropylcarbinyl system undergoes every possible rearrangement of small-ring compounds. Relief of ring strain provides a potent thermodynamic driving force for these processes and this can be usefully applied in organic synthesis[1].

During the course of our studies on the chemistry of strained polycyclic molecules that contain the cyclopropyl moiety[2–4], we have developed a simple synthesis of 9-substituted 2,8-didehydronoradamantane derivatives. We now wish to report the synthesis of 2,8-didehydronoradamantan-9-one (**2**), 2,8-didehydronoradamantan-9-ol (**3**), and tosylhydrazone **4**, and some of the aspects of their chemistry, particularly the cyclopropane ring-opening reactions under the influence of chemical reagents such as electrophiles, nucleophiles, and single electron donors.

Results and Discussion

As shown in Scheme 1, 2,8-didehydronoradamantan-9-one (**2**) was prepared by oxa-di-π-methane photorearrangement of brend-4-en-2-one (**1**). Irradiation of ketone **1** in acetone solution with a high pressure mercury lamp through a Pyrex filter afforded 2,8-didehydronoradamantan-9-one (**2**) along with a small amount of the reduction product, brendan-2-one.

The main product, ketone **2**, was isolated in 25% yield. This suggested that a 1,3-acyl shift[5] could take place in competition with the oxa-di-π-methane photorearrangement, leading to the enantiomer of **1**. Therefore, we prepared the deuterated ketone **1a**[6], which, in the case of a 1,3-acyl shift, should give the isotopomer **1b**. Irradiation of ketone **1a** for 15 min afforded a mixture of five products: the brendenones **1a** and **1b**, [2-D]2,8-didehydronoradamantan-9-one (**2a**) and two brendan-2-ones (Scheme 2).

Reduction of **2** with lithium aluminum hydride gave alcohol **3**. Treatment of **2** with tosylhydrazine afforded **4** in 92% yield. The structures of **2**, **3**, and **4** were determined from their spectral characteristics (vide infra).

When treated with a catalytic amount of perchloric acid in 80% aqueous acetone at 45°C for 48 h, 2,8-didehydronoradamantan-9-ol (**3**) rearranged to give *exo*-brend-4-en-2-ol (**5a**) in 76% yield. When the reaction was interrupted after 4 h, a mixture of three products was obtained: starting alcohol **3**, *exo*-2,4-didehydrobrendan-5-ol (**11**), and *exo*-brend-4-en-2-ol (**5a**). The structures of **11** and **5a** were unambiguously assigned by comparison of their IR and NMR spectra with the spectra of authentic samples[3].

The exclusive formation of *exo*-substituted alcohols **11** and **5a** supports the formation of bridged cations[8][9] **12** and **13** (Scheme 3). After complete conversion of **3**, the only product is **5a**, owing to its greater thermodynamic stability[10].

Similar results were obtained on treatment of **3** with thionyl chloride or $ZnCl_2$ under Mitsunobu conditions[11]: *exo*-2-chlorobrend-4-ene (**5b**) was produced in 47% and 36% yield, respectively.

Reaction of **3** with the 1:1 complex of dimethyl sulfide and *N*-chlorosuccinimide afforded **5b** in 46% yield.

These examples indicate that the 2,8-didehydronoradamantane skeleton has a high propensity toward rearrangement to brendyl products. This was also confirmed by the acid-catalysed rearrangement of **2**. When **2** was dissolved in glacial acetic acid in the presence of a catalytic amount of conc. H_2SO_4 or $HClO_4$ at 90°C, brend-4-en-2-one (**1**) was obtained in 65% yield. According to MO calculations[10] ketone **1** is more stable than ketone **2** by 18 kcal mol^{-1}.

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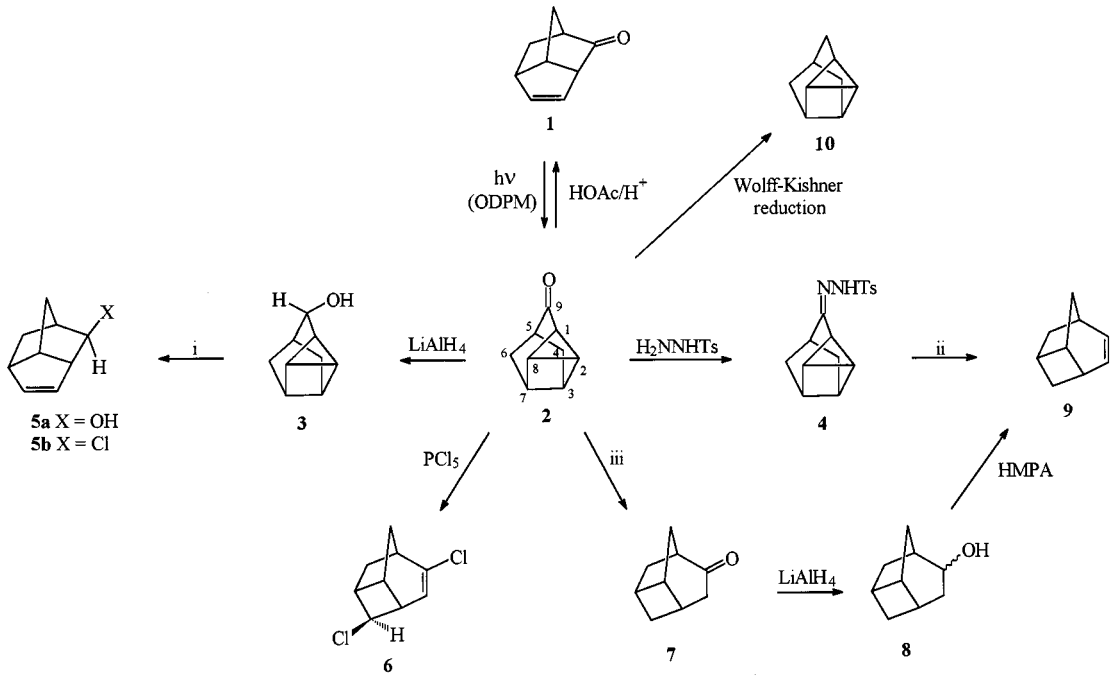
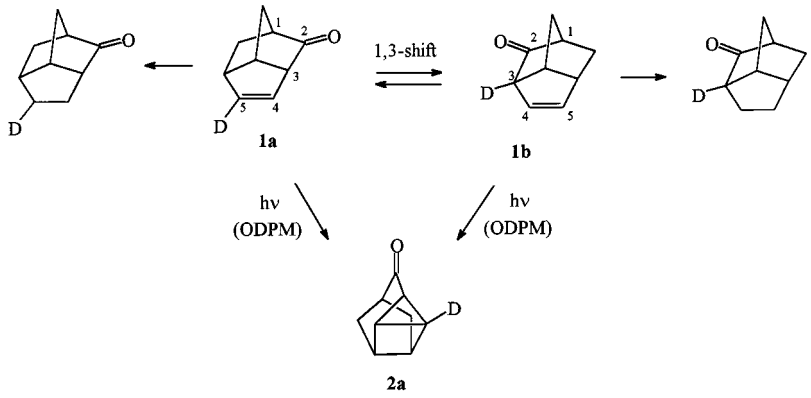
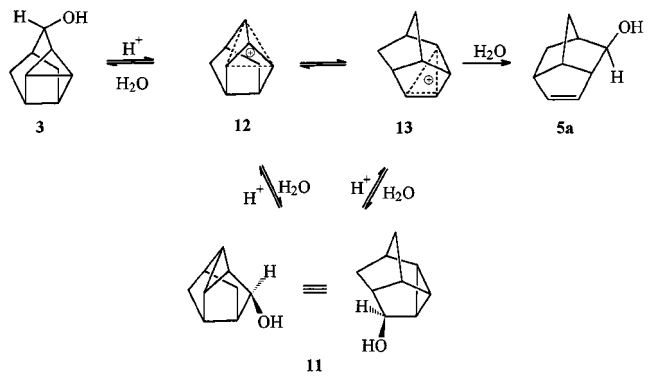


Scheme 1



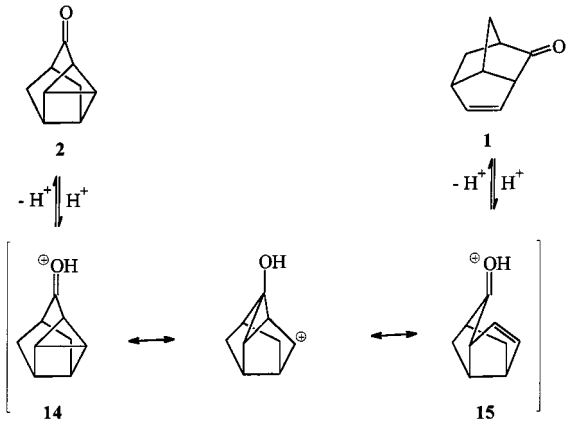
Scheme 2



Scheme 3

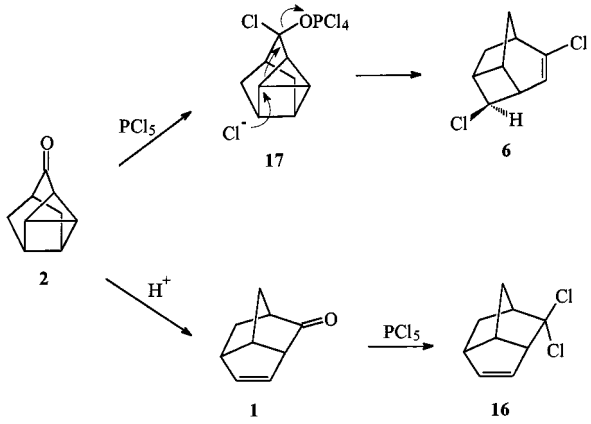
This rearrangement could be explained by the formation of oxonium ions **14** and **15**, as shown in Scheme 4. Thermodynamically controlled reactions allowing interconversion of these isomers thus give only brendyl product.

However, reaction of **2** with PCl_5 at room temperature afforded a mixture of two products in a 5:1 ratio, and the major product is not a brendyl derivative. The products were separated by MPLC and the major product was identified as *exo*-2,5-dichlorotricyclo[4.2.1.$0^{3,8}$]non-4-ene (**6**). The structure of dichloride **6** was obtained by 2D correlation NMR experiments (COSY and HETCOR) and proton coupled spectra. The minor product was identified as 2,2-dichlorobrend-4-ene (**16**). As shown in Scheme 5, the



Scheme 4

most likely reaction of **2** with PCl_5 is a concerted reaction, which involves formation of **17** followed by nucleophilic attack of the chloride ion. Formation of dichloride **16** could be explained by an acid-catalysed rearrangement[12] of **2** to ketone **1**, followed by reaction with PCl_5.



Scheme 5

The tricyclo[4.2.1.$0^{3,8}$]nonane skeleton was also obtained in the reactions that proceeded through formation of cyclopropylmethyl radical species. Electron transfer reduction of **2** with lithium in ammonia produced ketone **7** in 26% yield[4]. Similarly, irradiation of ketone **2** at 254 nm in acetonitrile in the presence of $LiClO_4$ and triethylamine, afforded **7** in 56% yield[13]. This approach provides straightforward synthetic access to tricyclo[4.2.1.$0^{3,8}$]nonane derivatives. $LiAlH_4$ reduction of ketone **7** afforded mixture of *exo*- and *endo*-alcohols **8** in a 1:11 ratio. Subsequent dehydration of **8** with HMPA at 230°C gave **9** as the sole product.

Likewise, olefin **9** was the only product in the reduction of tosylhydrazone **4** with both $NaBH_3CN$/TsOH and $BH_3 \times THF$. However, Wolff−Kishner reduction of ketone **2** gave the non-rearranged product, 2,8-didehydronoradamantane (**10**) as the sole product. The structures of all new hydrocarbons were established by spectroscopic means (see Experimental Section).

Conclusion

Novel 9-substituted 2,8-didehydronoradamantane derivatives **2**, **3**, and **4** have been synthesized and cyclopropane ring-opening reactions were studied. Acid-catalysed isomerization and nucleophilic substitution of **3** provide *exo*-2-substituted brend-4-ene derivatives exclusively, which supports the formation of a bridged bicyclobutonium ion. However, reaction of ketone **2** with PCl_5 proceeds by cleavage of the C-1−C-2 bond of **2** to give *exo*-2,5-dichlorotricyclo[4.2.1.$0^{3,8}$]non-4-ene (**6**). The tricyclo[4.2.1.$0^{3,8}$]nonane skeleton was also obtained by electron transfer reduction of **2** and by reduction of the corresponding tosylhydrazone **4** with boron hydrides. However, Wolf−Kishner reduction of **2** gave the non-rearranged product, 2,8-didehydronoradamantane (**10**). These results clearly show that the cyclopropane ring-opening reactions of cyclopropyl ketone **2** are very dependent upon the reaction conditions used. Electron transfer reduction of **2** provides a straightforward entry to various tricyclo[4.2.1.$0^{3,8}$]nonane derivatives.

Experimental Section

General Remarks: The purity of all compounds was assessed by capillary GLC. MPLC separation was conducted on a Merck Lobar column (LiChroprep-Si 60) in conjunction with a Fluid Metering INC pump and Waters Associates Model R403 differential refractometer detector. − Melting points were obtained on a Thiele apparatus and are uncorrected. − The ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini 300 spectrometer (300 MHz and 75.5 MHz, for ^{1}H and ^{13}C, respectively). − IR spectra were recorded with a Perkin−Elmer 297 spectrophotometer and high-resolution mass spectra were recorded on an Extrel FTMS 2001 spectrometer. − All chemicals, if not specified otherwise, were of commercial reagent grade and were used without further purification.

2,8-Didehydronoradamantan-9-one (2): A solution of 200 mg (1.5 mmol) of ketone **1** in 350 mL of acetone was purged with N_2 and then irradiated with a high-pressure mercury lamp (400 W) through a Pyrex filter. The reaction was followed by GLC. After 1 h of irradiation, ketone **1** had reacted completely and the acetone was distilled off. The yellow residue was chromatographed on silica gel, using 0−10% ether in pentane as an eluant, to afford 50 mg (25%) of **2** as a waxy solid and 15 mg (7%) of brendan-2-one[14]. Spectral data for **2**: IR (KBr): $\tilde{\nu}$ = 3035 (w) cm^{-1}, 2950 (s), 2920 (s), 2850 (m), 1695 (s). − ^{1}H NMR ($CDCl_3$): δ = 1.48−1.60 (m, 3 H), 1.95 (d, *J* = 12.6 Hz, 2 H), 2.45−2.49 (m, 2 H), 2.74 (m, 1 H), 2.97 (br.s, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 26.4 (d, C-1), 31.6 (d, 2 C, C-2 and C-8), 34.1 (d, 2 C, C-3 and C-7), 38.2 (t, 2 C, C-4 and C-6), 51.8 (d, C-5), 211.3 (s, C-9). − MS (70 eV); *m*/*z* (%): 134 (24) [M$^+$], 116 (47), 115 (33), 91 (100), 78 (92). − $C_9H_{10}O$ (134.2): calcd. C 80.56, H 7.51; found C 80.42, H 7.44.

Irradiation of [5-D]Brend-4-en-2-one (1a): A solution of 160 mg (1.19 mmol) of ketone **1a** in 350 mL of acetone was purged with N_2 and then irradiated for 15 min with a high-pressure mercury lamp (400 W) through a Pyrex filter. The acetone was distilled off and the residue was chromatographed on neutral Al_2O_3, using 0−10% ether in pentane as an eluant, to afford 27 mg (17%) of ketone **2a** and 88 mg of a mixture of the deuterated isomers of brendan-2-one and brend-4-en-2-one. The mixture of unsaturated

ketones **1a** and **1b** was separated from isotopomers of brendan-2-one by column chromatography on 5% $AgNO_3$-pretreated Al_2O_3 using 0−10% ether in pentane as the eluant. 12 mg (7.5%) of a mixture of [3-D]brendan-2-one and [5-D]brendan-2-one in a 1:1.5 ratio, and 58 mg (36.3%) of a mixture of [3-D]brend-4-en-2-one (**1b**) and [5-D]brend-4-en-2-one (**1a**) in a 1:1.5 ratio, were obtained respectively. The ratio of **1a** to **1b**, as well as the ratio of saturated isotopomers, was estimated from quantitative ^{13}C-NMR spectra.

2,8-Didehydronoradamantan-9-ol (3): A solution of 175 mg (1.31 mmol) of **2** in 10 mL of dry ether was added dropwise to a stirred suspension of 57 mg (1.31 mmol) of $LiAlH_4$ in 10 mL of dry ether. The reaction mixture was refluxed for 4 h, cooled to room temp., and diluted with 7 mL of ether. The excess $LiAlH_4$ was destroyed by careful addition of water (30 mL). The ether layer was separated and the water layer was extracted with ether (3× 20 mL). The ether extracts were combined and dried with anhydrous $MgSO_4$. Evaporation of the solvent afforded 160 mg (90%) of alcohol **3**, m.p. 113−116°C. − IR (KBr): $\tilde{\nu}$ = 3350 (s, OH) cm^{-1}, 3040 (m), 2930 (s), 2850 (m). − ^1H NMR ($CDCl_3$): δ = 0.81 (m, 1 H), 0.94 (m, 1 H), 1.15 (m, 1 H), 1.41 (d, *J* = 12.2 Hz, 1 H), 1.68−1.83 (m, 4 H), 2.23 (m, 1 H), 2.63 (br.s, 2 H), 4.14 (dd, *J* = 3.4 and 3.3 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 18.6 (d), 19.1 (d), 19.2 (d), 26.1 (t), 31.8 (d), 32.4 (d), 33.2 (t), 41.9 (d), 68.3 (d). − MS (70 eV), *m*/*z* (%): 136 (6) [M^+], 117 (100), 91 (23), 80 (35), 79 (45), 77 (20). − HRMS: calcd. for $C_9H_{12}O$ 136.088815; found 136.088282. − $C_9H_{12}O$ (136.2): calcd. C 79.37, H 8.88; found C 79.49, H 9.04.

Reaction of Alcohol 3 with $HClO_4$ in 80% Aqueous Acetone: To a stirred solution of 50 mg (0.37 mmol) of **3** in 10 mL of 80% aqueous acetone, was added one drop of 70% $HClO_4$. The reaction mixture was stirred for 48 h at ca. 45°C. After evaporation of the acetone the residue was treated with saturated $NaHCO_3$ solution (10 mL), then saturated with NaCl, and extracted with ether (4× 5 mL). The combined ether extracts were dried with anhydrous $MgSO_4$. Evaporation of the solvent afforded 38 mg (76%) of *exo*-brend-4-en-2-ol (**5a**)[15]. When the acid-catalysed rearrangement of **3** was interrupted prior to complete conversion of **3** (i.e. after 4 h), a mixture of three products was obtained after work up. Chromatography on a silica gel column, using 0−10% ether in pentane as the eluant, afforded 13 mg (26%) of *exo*-2,4-didehydrobrendan-5-ole (**11**)[15], 8 mg (16%) of brend-4-en-2-ol (**5a**)[15], and 24 mg (48%) of alcohol **3**.

Reaction of Alcohol 3 with $SOCl_2$: A mixture of 45 mg (0.33 mmol) of 2,8-didehydronoradamantan-9-ol (**3**) and 1.5 mL of $SOCl_2$ was stirred for 1.5 h at room temp. The excess $SOCl_2$ was evaporated and 10 mL of water was added. The reaction mixture was extracted with pentane (4× 5 mL) and the combined extracts were dried with anhydrous $MgSO_4$. After evaporation of the pentane the residue was chromatographed on silica gel with pentane as the eluent to give 24 mg (47%) of *exo*-2-chlorobrend-4-ene (**5b**)[15].

Reaction of Alcohol 3 with $ZnCl_2$/Ph_3P/DEAD: A mixture of 50 mg (0.37 mmol) of 2,8-didehydronoradamantan-9-ol (**3**), 212 mg (0.8 mmol) of Ph_3P, and 41 mg (0.30 mmol) of $ZnCl_2$ in 2 mL of dry toluene was stirred for 10 min at room temp., and then 0.13 mL (0.8 mmol) of diethyl azodicarboxylate (DEAD) was added slowly. The reaction mixture was stirred for 2 h at room temp., and then chromatographed on silica gel, with pentane as the eluant, to give 20 mg (36%) of *exo*-2-chlorobrend-4-ene (**5b**)[15].

Reaction of Alcohol 3 with $(CH_3)_2S$/NCS: To a stirred, cooled (ice/water) solution of 67 mg (0.50 mmol) of *N*-chlorosuccinimide (NCS) in 3 mL of dry CH_2Cl_2, under N_2, was added 0.041 mL (0.55 mmol) of dimethyl sulfide. The solution was then cooled to −15°C and 48 mg (0.35 mmol) of 2,8-didehydronoradamantan-9-ol (**3**) in 1 mL of dry CH_2Cl_2 was added over 10 min. The cooling bath was removed and reaction mixture was stirred for 3 h under N_2 and then poured into cold water (10 mL). The reaction mixture was extracted with ether (4× 5 mL) and the combined extracts were dried with anhydrous $MgSO_4$. After evaporation of the solvent the residue was filtered through a short column of silica gel, with pentane as the eluant, to give 25 mg (46%) of *exo*-2-chlorobrend-4-ene (**5b**)[15].

Reaction of Ketone 2 with H_2SO_4 or $HClO_4$ in CH_3COOH: To a solution of 50 mg (0.37 mmol) of 2,8-didehydronoradamantan-9-one (**2**) in 5 mL of glacial acetic acid, was added one drop of H_2SO_4 or $HClO_4$. The reaction mixture was refluxed for 4 h, cooled to room temp., and diluted with 20 mL of water. The mixture was extracted with ether (3× 10 mL), the combined extracts were washed with saturated $NaHCO_3$ solution, water, and dried with anhydrous $MgSO_4$. Evaporation of the solvent afforded 32 mg (65%) of brend-4-en-2-one (**1**).

Reaction of Ketone 2 with PCl_5: To a stirred, cooled (ice/water) solution of 73 mg (0.54 mmol) of 2,8-didehydronoradamantan-9-one (**2**) in 2.5 mL of CCl_4, was added 175 mg (0.85 mmol) of PCl_5. The reaction mixture was stirred overnight at room temp., and then poured onto 10 g of ice. The mixture was extracted with pentane (4× 20 mL) and the combined extracts were dried with anhydrous $MgSO_4$. Evaporation of the solvent afforded 60 mg (45%) of a mixture of two products in a ratio of 5:1 (GLC, capillary column DB−210, 120°C). After MPLC separation, with hexane as the eluant, the main product was identified as *exo*-2,5-dichlorotricyclo[4.2.1.$0^{3,8}$]non-4-ene (**6**) and the minor product as 2,2-dichlorobrend-4-ene (**16**). Spectral data for **6**, waxy solid: − IR (KBr): $\tilde{\nu}$ = 2980 (s) cm^{-1}, 2925 (s), 2860 (m), 1630 (m, C=C), 1015 (s), 725 (m). − ^1H NMR ($CDCl_3$): δ = 1.50−1.70 (m, 2 H), 1.85−2.05 (m, 2 H), 2.74−2.87 (m, 2 H), 2.96 (dd, *J* = 12.3 and 6.8 Hz, 1 H), 3.50 (m, 1 H), 3.68 (s, 1 H), 5.89 (d, *J* = 6.8 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 35.7 (t), 36.1 (d), 40.2 (t), 45.2 (d), 46.5 (d), 48.4 (d), 63.8 (d), 122.3 (d), 142.5 (s). − HRMS: calcd. for $C_9H_{10}Cl_2$ 188.015956; found 188.012093.

Preparation of Tosylhydrazone 4: A mixture of 64 mg (0.48 mmol) of ketone **2** and 93 mg (0.50 mmol) of *p*TsHNNH$_2$ in 1.5 mL of dry ethanol was stirred at 50°C for 1 h, cooled to room temperature and then left in a refrigerator overnight. To the resulting suspension was added 30 mL of water. The mixture was extracted with ether (3× 15 mL) and the combined extracts were dried with anhydrous $MgSO_4$. The solvent was evaporated to give 132 mg (92%) of tosylhydrazone **4**, as a white solid, m.p. 173−177°C. − IR (KBr): $\tilde{\nu}$ = 3240 cm^{-1} (s), 3040 (w), 3000 (w), 2980 (s), 2950 (m), 2920 (m), 2850 (w), 1645 (m), 1600 (m), 1330 (vs), 1165 (vs). − ^1H NMR ($CDCl_3$): δ = 1.18−1.34 (m), 1.54−1.78 (m), 2.10−2.14 (m), 2.20−2.25 (m), 2.36−2.48 (m, with distinguishable singlet at 2.43 ppm, CH_3), 3.28−3.30 (m), 7.31 (d, *J* = 8.0 Hz), 7.86 (d, *J* = 8.0 Hz). − ^{13}C NMR ($CDCl_3$): δ = 14.6, 21.2, 26.4, 28.3, 33.6, 35.4, 36.0, 36.7, 44.5, 127.9, 129.3, 135.4, 143.5, 167.8. − $C_{16}H_{18}N_2O_2S$ (302.1): calcd.C 63.55, H 6.00, N 9.26; found C 63.37, H 5.91, N 9.19.

Reduction of Tosylhydrazone 4 with BH_3 × THF: To an ice-cooled solution of 132 mg (0.44 mmol) of tosylhydrazone **4** in 2.5 mL of dry THF was added 1 mL (ca. 1 mmol) of a 1 M solution of BH_3 × THF under N_2. After stirring for 15 min, the ice/water bath was removed and reaction mixture was stirred for 1 h at room temperature, and then 1 mL of water and 0.7 mL of 5 M NaOH was added. The stirring was continued at room temperature for 1 h and then an additional 10 mL of water was added. The mixture was extracted with pentane (3× 10 mL) and the combined extracts were dried with anhydrous $MgSO_4$. The solution was concentrated in

vacuo and filtered through a short column of alumina (activity I), with pentane as the eluant, to give 11 mg (21%) of hydrocarbon **9** as a very volatile substance. An analytical sample (waxy solid) was obtained by sublimation at atmospheric pressure and at room temperature using a dry-ice finger-trap. − IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1} (w), 2930 (s), 2850 (m). − ^1H NMR ($CDCl_3$): δ = 1.20−1.80 (m, 5 H), 2.45−2.74 (m, 4 H), 3.00 (m, 1 H), 5.88 (dd, *J* = 8.8 and 6.2 Hz, 1 H), 6.32 (dd, *J* = 8.8 and 8.4 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 34.3 (d), 35.9 (t, 2 C), 37.3 (d), 37.9 (d), 38.5 (d), 40.2 (t), 131.9 (d), 137.4 (d). − HRMS: calcd. for C_9H_{12} 120.093900; found 120.093831.

Reduction of Tosylhydrazone 4 with $NaBH_3CN$/*p*TsOH/HMPA: A solution of 300 mg (1.0 mmol) of tosylhydrazone **4**, 315 mg (5 mmol) of $NaBH_3CN$, 50 mg of *p*TsOH and 5 mL of HMPA was heated at 180°C for 5 h. During this time the product sublimed. The sublimate was washed off with $CDCl_3$ directly into an NMR tube and identified, by comparison of its ^1H- and ^{13}C-NMR spectra with the spectra of an authentic sample, as tricyclo[4.2.1.$0^{3,8}$]non-4-ene (**9**).

Wolff−Kishner Reduction of 2,8-Didehydronoradamantan-9-one (2): A solution of 200 mg (1.5 mmol) of ketone **2**, 10 mL of diethylene glycol, 0.4 mL (8.0 mmol) of 98−100% hydrazine hydrate and 280 mg (5.0 mmol) of KOH was heated at 100°C for 2 h and then at 210°C for 5 h. During this time the product sublimed. The sublimate was dissolved in pentane (20 mL) and dried with anhydrous $MgSO_4$. The pentane was evaporated to give 120 mg (67%) of 2,8-didehydronoradamantane (**10**) as a white waxy solid. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w), 3010 (w), 2960 (s), 2920 (s), 2850 (s), 1435 (m), 1290 (m), 1255 (m), 875 (s), 770 (s), 720 (m). − ^1H NMR ($CDCl_3$): δ = 0.72 (br.s, 1 H, 1-H), 0.93−1.01 (m, 2 H, 4-H_{exo} and 6-H_{exo}), 1.39 (d, 2 H, *J* = 11.7 Hz, 4-H_{endo} and 6-H_{endo}), 1.55−1.59 (m, 2 H, 2-H and 8-H), 1.88 (br.s, 2 H, 9-H), 2.20 (br.s, 1 H, 5-H), 2.64 (br.s, 2 H, 3-H and 7-H). − ^{13}C NMR ($CDCl_3$): δ = 12.9 (d, 1 C, C-1), 18.0 (d, 2 C, C-2 and C-8), 29.2 (t, 1 C, C-9), 33.2 (t, 2 C, C-4 and C-6), 33.7 (d, 2 C, C-3 and C-7), 35.0 (d, 1 C, C-5). − C_9H_{12} (120.2): calcd. C 89.93, H 10.07; found C 89.73, H 10.12.

Photochemically Induced Electron Transfer Reduction of Ketone 2: A solution of 83 mg (0.61 mmol) of 2,8-didehydronoradamantan-9-one (**2**), 0.88 mL (6.1 mmol) of Et_3N and 67 mg (0.61 mmol) of $LiClO_4$ in 22.5 mL of dry CH_3CN was irradiated during 24 h in a Rayonet reactor equipped with sixteen 254 nm lamps. The solvent was evaporated and the residue was chromatographed on silica gel using 0−10% of diethyl ether in pentane as the eluant. The first chromatography fractions afforded 46 mg (56%) of tricyclo[4.2.1.$0^{3,8}$]nonan-5-one (**7**) as a waxy solid. Subsequent elution afforded 22 mg of the starting ketone **2**. Spectral data for tricyclo[4.2.1.$0^{3,8}$]nonan-5-one (**7**): − IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (s), 2850 (m), 1720 (s, C=O). − ^1H NMR ($CDCl_3$): δ = 1.05 (m, 1 H), 1.56 (ddd, *J* = 12.9, 4.3 and 4.2 Hz, 1 H), 1.69 (d, *J* = 13.2 Hz, 1 H), 1.92−1.98 (m, 2 H with distinguishable doublet at 1.94, *J* = 12.9 Hz), 2.18 (d, *J* = 17.0 Hz, 1 H), 2.47 (dd, *J* = 17.0 and 5.0 Hz, 1 H), 2.53−2.69 (m, 3 H), 2.87 (m, 1 H), 3.11 (m, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 26.8 (d), 30.7 (t), 33.4 (t), 34.7 (d), 36.5 (d), 38.1 (t), 40.4 (t), 52.4 (d), 217.2 (s). − HRMS: calcd. for $C_9H_{12}O$ 136.088815; found 136.089139.

Electron Transfer Reduction of Ketone 2 with Li/NH_3: A two-necked flask was fitted with a dry-ice reflux condenser and the flask was immersed into a dry-ice/acetone bath. A gentle stream of NH_3 gas was passed through the apparatus until 7 mL of liquid NH_3 was collected. To the liquid ammonia was added 42 mg of Li metal, in small pieces, until an intense blue color was obtained. A solution of 70 mg (0.52 mmol) of 2,8-didehydronoradamantan-9-one (**2**) in 1.5 mL of dry ether was then added dropwise. The dry-ice/acetone bath was replaced with an ice/water bath and the reaction mixture was stirred for 8 h. After evaporation of the NH_3, solid NH_4Cl was added to destroy the excess Li and then 20 mL of water was added. The mixture was extracted with ether (3× 10 mL) and the combined extracts were dried with anhydrous $MgSO_4$. After evaporation of the solvent the residue was chromatographed on silica gel, with 0−10% of ether in pentane as the eluant, to give 16 mg (26%) of tricyclo[4.2.1.$0^{3,8}$]nonan-5-one (**7**) as a waxy solid and 9 mg of starting ketone **2**.

Tricyclo[4.2.1.$0^{3,8}$]nonan-5-ols (8): A solution of 135 mg (1.0 mmol) of ketone **7** in 10 mL of dry ether was added to a stirred suspension of 38 mg (1.0 mmol) of $LiAlH_4$ in 10 mL of dry ether. The reaction mixture was refluxed for 5 h, cooled to room temp., and diluted with 7 mL of ether. The excess $LiAlH_4$ was destroyed by careful addition of water (30 mL). The ether layer was separated and the aqueous layer was extracted with ether (3× 20 mL). The ether extracts were combined and dried with anhydrous $MgSO_4$. The solvent was evaporated and the residue sublimed (60°C, 14 mbar) to afford 90 mg (70%) of a mixture of *endo*- and *exo*-alcohols **8** in a 92:8 ratio[16]. The ratio of isomers was determined by integration of the signals at δ = 4.38 and δ = 4.06 in the ^1H-NMR spectrum of the mixture of isomers. The isomers were not separated. − ^1H NMR ($CDCl_3$) of the mixture of isomers: δ = 1.20−1.55 (m), 1.82−1.92 (m), 1.98 (d, *J* = 13.5 Hz), 2.16−2.20 (m), 2.35−2.47 (m), 2.50−2.60 (m), 2.71−2.77 (m), 4.06 (dd, *J* = 8.1 and 7.9 Hz, **H**-COH of *exo*-**8**), 4.38 (dd, *J* = 7.8 and 7.6 Hz, **H**-COH of *endo*-**8**). − ^{13}C NMR ($CDCl_3$) of *endo*-**8**: δ = 30.6 (t), 31.1 (t), 31.2 (d), 31.7 (t), 32.4 (t), 34.4 (d), 36.3 (d), 41.4 (d), 70.2 (d). − ^{13}C NMR ($CDCl_3$) of *exo*-**8**: δ = 28.1 (t), 28.6 (d), 30.9 (t), 32.0 (t), 34.8 (d), 37.0 (d), 38.4 (t), 45.3 (d), 73.2 (d).

Dehydration of Tricyclo[4.2.1.$0^{3,8}$]nonan-5-ols (8): A solution of 75 mg (0.55 mmol) of alcohols **8** in 2 mL of HMPA was heated at 230°C for 20 h, cooled to room temp., diluted with 50 mL of pentane, and washed with water (3× 25 mL). The pentane layer was dried with anhydrous $MgSO_4$. Evaporation of the solvent afforded 16 mg (24%) of tricyclo[4.2.1.$0^{3,8}$]non-4-ene (**9**).

2,2-Dichlorobrend-4-ene (16): To a cooled (ice/water) solution of 50 mg (0.37 mmol) of brend-4-en-2-one (**1**) in 2 mL of CCl_4 was added 120 mg (0.58 mmol) of PCl_5. The reaction mixture was stirred overnight at room temp., and then poured into 30 mL of cold water. The mixture was extracted with ether (3× 15 mL) and the combined extracts were dried with anhydrous $MgSO_4$. After evaporation of the solvent the residue was filtered through a column of silica gel, with pentane as the eluant, to give 30 mg (43%) of 2,2-dichlorobrend-4-ene (**16**) as a waxy solid. − IR (KBr): $\tilde{\nu}$ = 3060 (w) cm^{-1}, 2970 (s), 2880 (w), 2860 (w), 1470 (m), 1445 (m), 950 (m), 850 (s), 770 (s), 750 (s), 720 (s). − ^1H NMR ($CDCl_3$): δ = 1.57 (m, 1 H), 1.64 (d, *J* = 11.0 Hz, 1 H), 1.77 (d, *J* = 12.9 Hz, 1 H), 2.32 (d, *J* = 11.0 Hz, 1 H), 2.48 (m, 1 H), 2.84 (br.s, 1 H), 3.09 (br.s, 2 H), 5.90 (dd, *J* = 5.4 and 3.0 Hz, 1 H), 6.18 (dd, *J* = 5.4 and 3.1 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 32.8 (t), 35.4 (t), 41.4 (d), 53.8 (d), 59.0 (d), 61.2 (d), 95.8 (s), 134.2 (d) 141.3 (d). − HRMS: calcd. for $C_9H_{10}Cl_2$ 188.015956; found 188.015777.

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[9] Cation **13** is more stable than **12** by ca. 0.6 kcal mol^{-1}, and the final product arises from **13**. Under the same conditions both alcohols *exo*-**11** and *endo*-**11** rearrange to give *exo*-brend-4-en-2-ol (**5a**). For the chemistry of **11** → **5a** see ref.[3]
[10] The enthalpies of formation (ΔH_f) for optimised geometries of **1**, **2**, **3**, **5a**, and **11** were calculated to be −12.26, 5.73, −4.82, −24.07, and −9.60 kcal mol^{-1}, respectively. Calculations were performed by the PM3 semiempirical molecular orbital method using the HyperChem 5.0 program package for Windows (Hypercube, Inc. Gainesville, FL, USA). Restricted Hartree−Fock minimisations were applied with a convergence limit of < 0.001. The Polak−Ribiere block diagonal algorithm was used for all minimisations to a root mean square gradient of < 0.01 kcal A^{-1} mol^{-1}.
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[15] The identity of **5a**, **5b** and **11** was established by comparison of their spectral data with the spectra of authentic samples prepared by an alternative route; see ref.[3]
[16] Since a large degree of steric hindrance exists at the *endo*-face of the carbonyl group in **7**, attack of the $LiAlH_4$ takes place from the *exo*-side to give *endo*-**8** as the major product.

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