7 (n = 6, 3.02 g), Raney nickel W-2[18] (prepared from 55 g of Raney alloy), and dioxane (100 mL) was refluxed for 1 h. After filtration and solvent evaporation, the residue was chromatographed on a short column of silica gel (benzene). The yield, after crystallization from methanol, was 2.52 g (90.2%): colorless plates; mp 100–100.5 °C (lit.[9] mp 99.6–100.6 °C).

Registry No. **3** (X = H; n = 2), 68114-93-2; **3** (X = H; n = 3), 6337-58-2; **3** (X = Br; n = 3), 68114-87-4; **3** (X = Cl; n = 3), 67442-67-5; **3** (X = Cl; n = 4), 67442-69-7; **3** (X = Cl; n = 5), 67442-71-1; **3** (X = Cl; n = 6), 67442-73-3; **3** (X = Cl; n = 7), 67442-75-5; **3** (X = Cl; n = 8), 67442-77-7; **3** (X = Cl; n = 10), 67442-79-9; **4** (n = 3), 67449-47-2; **4** (n = 4), 67449-48-3; **4** (n = 5), 67449-49-4; **4** (n = 6), 67449-50-7; **4** (n = 7), 67449-51-8; **4** (n = 8), 67449-52-9; **4** (n = 10), 67629-81-6; **5** (n = 2), 88686-37-7; **5** (n = 3), 88686-38-8; **5** (n = 4), 88686-39-9; **5** (n = 5), 88686-40-2; **5** (n = 6), 88686-41-3; **5** (n = 7), 88686-42-4; **5** (n = 8), 88686-43-5; **5** (n = 10), 88686-44-6; **6** (n = 3), 67449-60-9; **6** (n = 4), 67449-61-0; **6** (n = 5), 67449-62-1; **6** (n = 6), 67449-63-2; **6** (n = 7), 67449-64-3; **6** (n = 8), 67449-65-4; **6** (n = 10, 67449-66-5; **7** (n = 3), 67449-53-0; **7** (n = 4), 67449-54-1; **7** (n = 5), 67449-55-2; **7** (n = 6), 67449-56-3; **7** (n = 7), 67449-57-4; **7** (n = 8), 67449-58-5; **7** (n = 10), 67449-59-6; **8** (n = 6), 4384-23-0; glyoxal, 107-22-2; chloroacetyl chloride, 79-04-9; 1,7-diphenylheptane, 22906-09-8; sodium sulfide, 1313-82-2.

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Synthesis and Chemistry of 2,8-Disubstituted Noradamantanes

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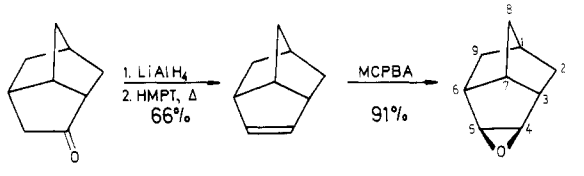
4,5-*exo*-Epoxybrendane (**3**) rearranged readily with sulfuric acid in acetone, and with boron trifluoride etherate in acetic acid, yielding, upon a hydrolytic workup, 86% of 2-*exo*-8-*exo*-noradamantanediol and 93% of 8-*exo*-acetoxy-2-*exo*-noradamantanol, respectively. Starting epoxide **3** was prepared in 60% overall yield from readily available 4-brendanone. Consequently, the acid solvolysis of **3** provides a convenient, general entry to the noradamantane system functionalized at carbons 2 and 8.

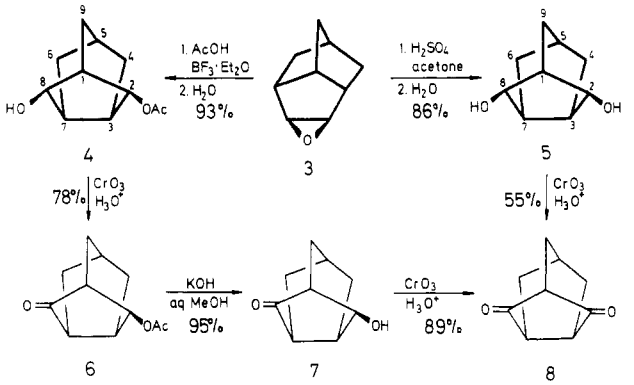
Noradamantane has attracted considerable attention since its first syntheses[1] due to its unique position as the next lower homologue of adamantane and the tricyclononane stabilomer.[2] Noradamantane derivatives have been used as starting materials for preparations of [2]diadamantane,[3a] dinoradamantanes,[3b] 5-substituted protoadamantanes,[3c] 9-substituted 9-homonoradamantanes,[3d] triaxanes,[3e] and ethanonoradamantanes,[3f] as well as substrates in numerous solvolytic,[3g] spectroscopic,[3h] carbene,[3i] and nitrene studies.[3j] The latter two led to unambiguous syntheses of adamantene and 2-azaadamantene.

Because of the lower symmetry of noradamantane compared to adamantane, five monosubstituted noradamantane isomers (1-, 2-*exo*-, 2-*endo*-, 3-, and 9-noradamantanes) are possible. All five noradamantanols and

Scheme I



Scheme II



their numerous derivatives are known.[4] However, only a few synthetic routes to disubstituted noradamantanes

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0022-3263/84/1949-1182$01.50/0

have been developed. Virtually all 2,6-,[5] 2,9-[6] and 3,7-disubstituted noradamantanes[7] were obtained by transannular ring closures of the corresponding disubstituted bicyclo[3.3.1]nonanes. 3,9-Disubstituted noradamantanes were prepared by Favorskii ring contraction of bridgehead-brominated 2,6-adamantanediones,[1a,8] while 2,4-disubstituted noradamantane derivatives were obtained by the intramolecular 1,3-dipolar cycloadditions of *C-endo*-bicyclo[3.2.1]oct-6-en-3-ylnitrones followed by the reductive cleavage of the resulting epoxyiminonoradamantanes.[9]

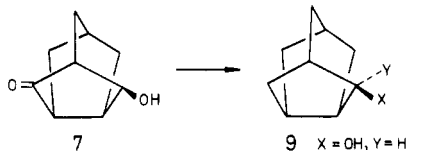
In the course of our studies of small-ring propellanes[10] we developed a facile, general, route to 2,8-disubstituted noradamantanes, which we report here. The key step was acid solvolysis of 4,5-epoxybrendane.

Results and Discussion

Our approach to 2,8-disubstituted noradamantanes is based on the acid-promoted rearrangement of deltacyclane to 2-noradamantanol reported by Nickon et al. as early as 1967.[1c] This rearrangement appears to involve the isomerization of the 4-brendyl cation to the 2-noradamantyl cation. Since noradamantane is the tricyclononane stabilomer,[2] it may be expected that suitable 4,5-disubstituted brendanes should rearrange, under appropriate conditions, to 2,8-disubstituted noradamantanes.

We chose 4,5-epoxybrendane (**3**) as the starting material. It was prepared in 60% overall yield from readily available 4-brendanone[11] (**1**) (Scheme I). Ketone **1** was reduced with $LiAlH_4$ to 4-brendanol,[12] which was dehydrated with HMPT at 215 °C.[14] The resulting crude olefin,[15] 4-brendene (**2**), was oxidized to 4,5-*exo*-epoxybrendane (**3**) with MCPBA in the usual manner. The ^{13}C NMR spectrum of **3** contained six signals indicating that it was one isomer rather than an exo–endo mixture. Its configuration was determined by ^1H NMR spectroscopy. The coupling constant of the vicinal hydrogen atoms H-4(5) and H-3(6) was 0.73 Hz, consistent with an angle of 90° between these atoms and, therefore, with the exo configuration of epoxide **3**.[16] This is in good agreement with the larger steric hindrance at the endo side of the starting olefin **2**, as well as with the exo,exo configuration of 2,8-disubstituted noradamantanes obtained by the acid solvolyses of **3** (vide infra).

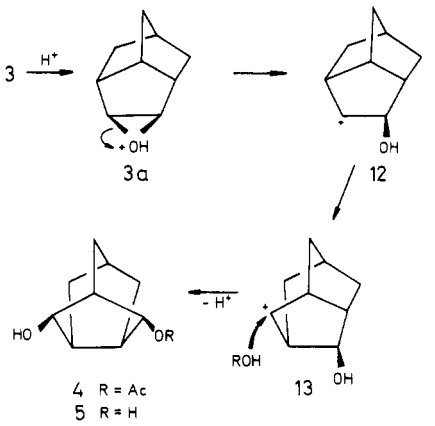
Scheme III[a]



7 9 X = OH, Y = H; 10 X = Y = O; 11 X = H, Y = OH

[a] 7 → 9: $TsNHNH_2$; $(PhCO)_2BH$; $NaOAc \cdot 3H_2O$ (30%). 9 → 10: CrO_3, H_3O^+ (87%). 10 → 11: $LiAlH_4$ (90%).

Scheme IV



4 R = Ac; 5 R = H; 13

4,5-*exo*-Epoxybrendane (**3**) rearranged readily at room temperature in the presence of an acid catalyst yielding, upon a hydrolytic workup, 2-*exo*-8-*exo*-disubstituted noradamantanes in high yields (Scheme II). Treatment of **3** with concentrated sulfuric acid in acetone produced 86% of pure 2-*exo*-8-*exo*-noradamantanediol (**5**). However, reaction of **3** with boron trifluoride etherate in acetic acid gave 93% of 8-*exo*-acetoxy-2-*exo*-noradamantanol (**4**) (90% pure by ^{13}C NMR). Hydrolysis of **4** with aqueous methanolic KOH yielded 87% of a diol, the ^{13}C NMR and ^1H NMR spectra of which were identical with those of noradamantanediol **5** obtained by sulfuric acid catalyzed rearrangement of **3**. The ^{13}C NMR spectrum of **5** contained only six signals indicating the same stereochemistry of both substituents. Jones oxidation of acetoxy alcohol **4** produced 78% of 8-*exo*-acetoxy-2-noradamantanone (**6**), which was subsequently hydrolyzed (95%) with aqueous methanolic KOH to 8-*exo*-hydroxy-2-noradamantanone (**7**). Hydroxy ketone **7** was readily oxidized (89%) with the Jones reagent to 2,8-noradamantanedione (**8**), which was proved to be identical with the product obtained by Jones oxidation of 2-*exo*-8-*exo*-noradamantanediol (**5**).

The stereochemistry of the substituents in 2,8-disubstituted noradamantanes **4** and **5** follows from the conversions of **4** to **5** and **4** to hydroxy ketone **7** (Scheme II), as well as from the reduction of **7** to the known alcohol, 2-*exo*-noradamantanol[1c,3f] (**9**) (Scheme III). Since this alcohol has not been fully characterized, we converted it into 2-*endo*-noradamantanol (**11**) by Jones oxidation followed by $LiAlH_4$ reduction of the resulting 2-noradamantanone (**10**).[17,18] The ^{13}C NMR, ^1H NMR, IR, and/or mass spectra of **9**, **10**, and **11** were consistent with the spectral data reported for these compounds.[1c,3f,18]

The proposed pathway of rearrangement of 4,5-*exo*-epoxybrendane (**3**) to 2-*exo*-8-*exo*-disubstituted nor-

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(11) Nickon, A.; Kwasnik, H. R.; Mathew, C. T.; Swartz, T. D.; Williams, R. O.; DiGiorgio, J. B. *J. Org. Chem.* **1978**, *43*, 3904.
(12) According to the ^{13}C NMR spectrum only one epimer was formed. The splitting pattern of the H-4 NMR signal is quite complex indicating it to be the endo epimer.[13] This is consistent with the larger steric hindrance at the endo face of the carbonyl group in **1**.
(13) Covey, D. F.; Nickon, A. *J. Org. Chem.* **1977**, *42*, 794.
(14) Monson, R. S.; Priest, D. N. *J. Org. Chem.* **1971**, *36*, 3826. Monson, R. S. *Tetrahedron Lett.* **1971**, 567. Arimatsu, S.; Yamaguchi, R.; Kawanisi, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1693.
(15) The ^{13}C NMR spectrum indicated the presence of approximately 10% of 2,4-didehydronoradamantane (triaxane).[3e]
(16) An inspection of molecular models of *exo*- and *endo*-4,5-epoxybrendane showed the angles between the vicinal hydrogen atoms H-4(5) and H-3(6) to be 90° and 30°, respectively.
(17) Ketone **10** is sterically less hindered at the exo face.
(18) Majerski, Z.; Šarac-Arneri, R.; Škare, D.; Lončar, B. *Synthesis* **1980**, 74.

adamantanes involves protonation of the oxygen atom to form **3a** (Scheme IV). The cleavage of either of the two carbon-oxygen bonds in **3a** leads to the 5-*exo*-hydroxy-4-brendyl cation (**12**), which rearranges subsequently by a 1,2-C,C shift to the thermodynamically more stable 8-*exo*-hydroxy-2-noradamantyl cation (**13**).[19] Since **13** is less hindered at the exo face, nucleophiles (ROH) will attack from this face to form 8-*exo*-substituted 2-*exo*-noradamantanols **4** (R = Ac) and **5** (R = H).[20]

In conclusion, acid solvolysis of 4,5-*exo*-epoxybrendane (**3**) provides a convenient, general, route to 2,8-disubstituted noradamantanes.

Experimental Section

The purity of all compounds was determined by GC and/or ^{13}C NMR. ^{13}C NMR and ^{1}H NMR spectra were acquired with a JEOL FX90Q spectrometer, IR spectra were recorded with a Perkin-Elmer 297 spectrophotometer, and mass spectra were obtained on a Varian CH-7 spectrometer. The quantitative analyses with ^{13}C NMR were performed by a combination of long pulse intervals (100 s) to assure complete relaxation of all ^{13}C nuclei and a gated decoupling, which eliminated the nuclear Overhauser enhancement.[21] GC analyses were carried out on a Varian Aerograph 1800 gas chromatograph. Melting points were determined, in sealed capillary tubes completely immersed in oil, by using a Thiele apparatus and were uncorrected. MCPBA was of technical grade and contained 85% of the active material. All other chemicals were of commercial reagent grade and were used without purification.

4-Brendanol.[12] A solution of 4-brendanone[11] (**1**) (1.9 g, 14 mmol) in dry ether (40 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (570 mg, 15 mmol) in dry ether (60 mL). The reaction mixture was stirred under reflux for 4 h. Wet ether (100 mL) was then added dropwise followed by the careful addition of water. The usual workup yielded 4-brendanol (1.77 g, 91.6%; ≥95% pure by ^{13}C NMR): mp 131–132 °C (lit.[22] 135–136 °C); ^{13}C NMR ($CDCl_3$) δ 74.6 (d), 46.5 (d), 45.6 (d), 42.8 (t), 42.5 (t), 39.6 (t), 36.8 (d), 35.5 (d), 29.2 (t); ^{1}H NMR ($CDCl_3$) δ 4.5–4.2 (complex m, 1 H), 2.6–0.9 (m, 13 H); IR (KBr) 3350, 2940, 2860, 1450, 1350, 1310, 1120, 1045 cm^{-1}; MS, *m/z* (relative intensity) 138 (M^+, 7), 120 (21), 94 (33), 92 (26), 91 (26), 79 (90), 77 (31), 70 (36), 67 (54), 66 (100). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.49; H, 10.39.

4-Brendene (2). A mixture of 4-brendanol (750 mg, 5.43 mmol) and HMPT (2.5 mL) was stirred at 210–215 °C for 5 h in a nitrogen atmosphere. After 2–3 h the product began to sublime. The sublimed material was dissolved in pentane. Evaporation of the solvent (without heating) yielded a very sublimable, waxy, solid (520 mg), which contained ~90% of **2** (468 mg, 72% based on 4-brendanol) and was used without purification in the next step. The spectral data of pure olefin **2** (≥98% by GC, DC-710, 80 °C; obtained by column chromatography on $AgNO_3$ (15%) pretreated silica gel using pentane followed by ether as the eluents) were consistent with the data reported[23] for 4-brendene. The melting point, however, was considerably lower: 84–86 °C (lit.[23] 178–180 °C). **2**: ^{13}C NMR ($CDCl_3$) δ 139.4 (d, 2 C), 54.0 (d, 1 C), 42.9 (d, 2 C), 42.1 (d, 1 C), 39.3 (t, 1 C), 36.1 (t, 2 C).

4,5-*exo*-Epoxybrendane (3). MCPBA (1.12 g, 5.52 mmol of the active material) was added in a few portions to a mixture of crude olefin **2** (520 mg,[15] 3.9 mmol of **2**), methylene chloride (40 mL), and 0.5 M aqueous $NaHCO_3$ solution (10 mL) and was stirred at room temperature. After 2 h the layers were separated, and the organic one was washed with 1 N aqueous NaOH solution (2 × 20 mL) followed by water (2 × 20 mL) and then dried ($MgSO_4$). The solvent was evaporated and the crude product was purified by column chromatography on neutral alumina (activity II/III). Elution with pentane–ether (3:1) yielded epoxide **3** (485 mg, 91.4% based on neat **2**; ≥98% pure by GC, DEGS, 160 °C): mp 173–176 °C; ^{13}C NMR ($CDCl_3$) δ 59.9 (d, 2 C), 39.7 (d, 2 C), 39.3 (d, 1 C), 36.6 (t, 1 C), 35.5 (d, 1 C), 33.3 (t, 2 C); ^{1}H NMR ($CDCl_3$) δ 3.33 (dd, $J_1 = J_2 = 0.73$ Hz, 2 H), 2.50–2.05 (m, 4 H), 1.72–1.33 (m, 4 H), 1.10–0.87 (m, 2 H); IR (KBr) 2940, 2865, 1443, 1400, 935, 848, 800, 622 cm^{-1}; MS, *m/z* (relative intensity) 136 (M^+, 1), 92 (48), 79 (43), 70 (100), 67 (48), 66 (38). Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.61; H, 8.75.

8-*exo*-Acetoxy-2-*exo*-noradamantanol (4). A few drops of boron trifluoride etherate were added to a solution of epoxide **3** (1.95 g, 14.3 mmol) in glacial acetic acid (30 mL) stirred at room temperature. After 30 min water (50 mL) was added and the product was extracted with chloroform (4 × 40 mL). The combined extracts were washed with saturated aqueous $NaHCO_3$ solution (3 × 30 mL) and dried ($MgSO_4$). Evaporation of the solvent yielded crude **4** (2.6 g, 92.8%; ~90% pure by ^{13}C NMR), which was purified by Kugelrohr distillation for the spectral analyses (~200 °C/14 mmHg; ≥95% pure by ^{13}C NMR): ^{13}C NMR ($CDCl_3$) δ 169.0 (s), 88.2 (d), 86.0 (d), 47.4 (d), 46.8 (d), 43.7 (d), 42.2 (t), 41.9 (t), 34.0 (d), 33.5 (t), 21.3 (q); ^{1}H NMR ($CDCl_3$) δ 4.99 (br s, 1 H), 3.87 (br s, 1 H), 3.2 (very br s, 1 H), 2.62 (br s, 2 H), 2.32 (br s, 1 H), 2.06 (s, 3 H), 2.09–1.91 (m, 1 H), 1.80–1.48 (m, 6 H); IR (neat) 3580, 3450, 2940, 2870, 1740, 1367, 1230, 1090, 1050 cm^{-1}; MS, *m/z* (relative intensity) 136 (M^+ – AcOH, 47), 107 (17), 92 (20), 79 (100), 66 (28), 58 (75). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.27; H, 8.05.

2-*exo*-8-*exo*-Noradamantanediol (5) was obtained by acid hydrolysis of **3** and by base hydrolysis of **4**.

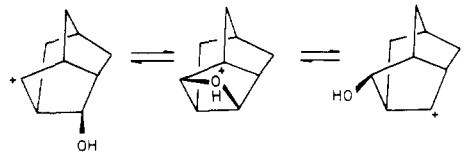
Acid Hydrolysis of 3. Concentrated sulfuric acid (0.1 mL) was added to a solution of **3** (400 mg, 2.94 mmol) in acetone (20 mL), which was stirred at room temperature. After 15 min, water (40 mL) was added and the product was extracted with chloroform (3 × 30 mL). The extracts were combined and dried ($MgSO_4$). Evaporation of the solvent yielded diol **5** (390 mg, 86.1%; pure by ^{13}C NMR): mp 234–235 °C; ^{13}C NMR ($CDCl_3$) δ 86.2 (d, 2 C), 48.4 (d, 1 C), 46.4 (d, 2 C), 41.7 (t, 2 C), 33.8 (d, 1 C), 33.2 (t, 1 C); ^{1}H NMR ($CDCl_3$) δ 4.89 (s, 2 H), 3.94 (s, 2 H), 2.59 (br s, 2 H), 2.36 (br s, 1 H), 1.96 (br s, 1 H), 1.8–1.4 (m, 6 H); IR (KBr) 3380, 2950, 2930, 2870, 1440, 1085, 1058 cm^{-1}; MS, *m/z* (relative intensity) 154 (M^+, 0.5), 136 (26), 118 (8), 107 (13), 92 (16), 80 (27), 79 (100), 66 (24), 58 (56). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.37; H, 9.19.

Base Hydrolysis of 4. A mixture of **4** (182 mg, 0.93 mmol), 50% aqueous methanol (10 mL), and potassium hydroxide (150 mg, 2.7 mmol) was stirred for 3 h at room temperature. The product was extracted with chloroform (3 × 10 mL). The extracts were combined and dried ($MgSO_4$). Evaporation of the solvent yielded diol **5** (125 mg, 87.3%; ~95% pure by ^{13}C NMR), the spectra of which were identical with those of the diol obtained by the acid hydrolysis of **3**.

8-*exo*-Acetoxy-2-noradamantanone (6). To a solution of **4** (670 mg, 3.42 mmol) in acetone (20 mL) stirred at room temperature the Jones reagent was added dropwise until a permanent red color appeared. The reaction mixture was stirred for an additional 10 min, then diluted with water (20 mL), and extracted with chloroform (3 × 30 mL). The extracts were combined and dried ($MgSO_4$). The solvent was evaporated and the crude product was purified by column chromatography on neutral alumina

(19) As both cations **12** and **13** are secondary, their relative thermodynamic stabilities should roughly parallel the relative stabilities of the corresponding hydrocarbons. Empirical force field calculations predicted noradamantane to be 2.5 (Engler's force field) or 5 kcal/mol (Allinger's force field) more stable than brendane.[2]

(20) The reaction pathway, in fact, appears to be more complex. Experiments with specifically deuterated epoxide **3** showed deuterium scrambling[10c] indicating a rapid degenerate isomerization of cation **13**, presumably via oxonium intermediate **14**:



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(activity II/III). Elution with pentane–ether (3:1) yielded acetoxy ketone **6** (520 mg, 78.4%; ≥95% pure by ^{13}C NMR): mp 56–57 °C; ^{13}C NMR ($CDCl_3$) δ 216.1 (s), 169.8 (s), 79.5 (d), 52.6 (d), 46.4 (d), 45.7 (t), 41.5 (d), 39.4 (t), 36.5 (t), 34.1 (d), 21.1 (q); ^1H NMR ($CDCl_3$) δ 4.81 (s, 1 H), 2.9–1.8 (m, 13 H, maximum at δ 2.00); IR (KBr) 2945, 2870, 1740, 1240, 1230, 1215, 1065, 1025 cm^{-1}; MS, *m/z* (relative intensity) 194 (M^+, 6), 152 (21), 134 (5), 80 (100), 79 (25), 73 (21). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.19; H, 6.98.

8-*exo*-Hydroxy-2-noradamantanone (7). A mixture of **6** (242 mg, 1.25 mmol), 50% aqueous methanol (15 mL), and potassium hydroxide (175 mg, 3.12 mmol) was stirred for 3 h at room temperature. The resulting mixture was saturated with sodium chloride and extracted with chloroform (3 × 30 mL). The extracts were combined and dried ($MgSO_4$). Evaporation of the solvent yielded hydroxy ketone **7** (180 mg, 94.7%; ≥95% pure by ^{13}C NMR): mp 248–250 °C; ^{13}C NMR ($CDCl_3$) δ 219.7 (s), 77.0 (d), 55.2 (d), 46.3 (d), 45.4 (t), 44.0 (d), 38.8 (t), 36.2 (t), 33.9 (d); ^1H NMR ($CDCl_3$) δ 3.92 (s, 1 H), 3.66 (br s, 1 H), 2.8–1.6 (m, 10 H, maximum at δ 1.80); IR (KBr) 3400, 2940, 2860, 1750, 1445, 1070, 1030 cm^{-1}; MS, *m/z* (relative intensity) 152 (M^+, 6), 134 (1), 94 (5), 80 (100), 79 (33), 73 (35), 67 (12). Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.23; H, 8.24.

2,8-Noradamantanedione (**8**) was prepared in 89% and 55% yield by Jones oxidation of **7** and **5**, respectively, following the procedure described for **6**. However, the crude product was purified by sublimation rather than column chromatography. **8** (pure by ^{13}C NMR): mp 211–213 °C; ^{13}C NMR ($CDCl_3$) δ 209.4 (s, 2 C), 64.0 (d, 1 C), 52.4 (d, 2 C), 45.8 (t, 2 C), 44.5 (t, 1 C), 35.0 (d, 1 C); ^1H NMR ($CDCl_3$) δ 3.17–2.82 (m, 3 H), 2.63–2.11 (m, 7 H, maximum at δ 2.29); IR (KBr) 2943, 2875, 1775, 1730, 1450, 1218, 1054, 873, 798 cm^{-1}; MS, *m/z* (relative intensity) 150 (M^+, 41), 94 (23), 80 (64), 79 (39), 78 (21), 67 (38), 66 (100), 55 (41). Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 72.05; H, 6.92.

2-*exo*-Noradamantanol (9). A solution of hydroxy ketone **7** (650 mg, 4.3 mmol) and tosylhydrazine (880 mg, 4.7 mmol) in methanol (10 mL) was stirred for 12 h at room temperature. Evaporation of the solvent yielded the crude hydroxy tosylhydrazone **7a**, which was used without purification in the next step.

A 1.9 M solution of diborane in dry THF (3.6 mL) was added to a solution of benzoic acid (1.0 g, 8.2 mmol) in chloroform (10 mL) stirred at 0 °C. After 10 min, a solution of the hydroxy tosylhydrazone **7a** in chloroform (3 mL) was added and the resulting mixture was stirred for an additional hour at 0 °C. Sodium acetate trihydrate (2.7 g, 19.8 mmol) was added afterward and the reaction mixture was stirred overnight at room temperature. Water (30 mL) was then added followed by ether (50 mL). The organic layer was separated, washed with saturated aqueous $NaHCO_3$ solution (5 × 30 mL), and dried ($MgSO_4$). The solvent was evaporated and the crude product was purified by column chromatography on neutral alumina (activity II/III). Elution with pentane–ether (1:0 to 1:1) yielded alcohol **9** (180 mg, 30% based on **7**; ≥98% pure by GC, DEGS, 170 °C). The ^1H NMR and IR spectral data were consistent with those reported[3f] for 2-*exo*-noradamantanol. **9**: ^{13}C NMR ($CDCl_3$) δ 83.7 (d), 46.2 (d), 43.6 (t), 43.4 (d), 41.3 (t), 39.1 (t), 36.3 (d), 35.1 (d), 34.5 (t); MS, *m/z* (relative intensity) 138 (M^+, 5), 120 (22), 92 (20), 91 (25), 79 (100), 78 (45), 67 (36), 66 (28).

2-Noradamantanone (10). Alcohol **9** (170 mg, 1.23 mmol) was oxidized by the procedure described for **6**. The crude product was purified by column chromatography on neutral alumina (activity II/III). Elution with pentane–ether (3:1) yielded ketone **10** (145 mg, 86.7%; ≥98% pure by GC, DEGS, 170 °C), the spectral data of which were in complete agreement with those reported previously.[18]

2-*endo*-Noradamantanol (11) was obtained in 90% yield by $LiAlH_4$ reduction of **10** following the procedure described for 4-brendanol. **11**: ^{13}C NMR ($CDCl_3$) δ 77.2 (d), 43.5 (t), 40.5 (d), 40.0 (d), 38.1 (t), 37.2 (d), 35.9 (d), 33.3 (t), 30.3 (t); ^1H NMR ($CDCl_3$) δ 4.05 (dd, J_1 = 5.8 Hz, J_2 = 3.2 Hz, 1 H), 2.5–1.1 (m, 13 H); IR (KBr) 3280, 2920, 2860, 1455, 1350, 1310, 1295 , 1145, 1100, 1040 cm^{-1}; MS, *m/z* (relative intensity) 138 (M^+, 4), 120 (19), 92 (20), 91 (26), 79 (100), 78 (41), 67 (40), 66 (32).

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Registry No. **1**, 1521-78-4; **2**, 88685-69-2; **3**, 88685-70-5; **4**, 88703-07-5; **5**, 88685-71-6; **6**, 88685-72-7; **7**, 88685-73-8; **7a**, 88685-74-9; **8**, 88685-75-0; **9**, 18117-75-4; **10**, 17931-67-8; **11**, 18117-74-3; 4-brendanol, 88762-77-0.

Stereodynamics of Substituted Neopentanes

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tert-Butyl rotation barriers have been measured in four monosubstituted neopentanes (Me_3CCH_2X, X = Me, Cl, Br, I) by using 270-MHz ^1H dynamic NMR spectroscopy. The barrier depends on X in the order: Me < Cl ~ Br ~ I. As a complement to the experimental DNMR data, Allinger's MM2 molecular mechanics program (1980 force field) was used to calculate optimized equilibrium geometries and *tert*-butyl rotation barriers for the four compounds. The MM2 barriers are compared to previously reported MM1 barriers.

Neopentyl systems have been important in the study of steric effects on the rate of a variety of reactions. Since it has been demonstrated that the rotation barrier about the quaternary carbon–secondary carbon bond in neopentyl[2–4] and related systems [i.e., $Me_2C(CH_2X)_2$, $MeC(CH_2X)_3$, X = Me, halogen][5] is accessible to the ^1H or $^{13}C\{^1H\}$ dynamic nuclear magnetic resonance (DNMR) method, the neopentyl systems constitute simple, experimentally accessible models for the *tert*-butyl rotation process.

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