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# SYNTHESIS OF ADAMANTANE DERIVATIVES—38[1]

## SYNTHESIS OF 1,3-BISHOADAMANTANE VIA RING-EXPANSION OF HOMOADAMANTAN-2-ONE AND HOMOADAMANT-4-EN-2-ONE

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**Abstract**—The ring expansion of homoadamant-4-en-2-one (7) *via* the corresponding aminomethyl alcohol (9) gave 1,3-bishomoadamant-7-en-4-one (10) as the major product which was converted to 1,3-bishomoadamant-4-ene (14) and 1,3-bishomoadamanta-4,7-diene (16) via the alcohols 13 and 15. Catalytic hydrogenation of 14 and 16 afforded 1,3-bishomoadamantane (2). The ring expansion of homoadamantan-2-one (17) via the aminomethyl alcohol (19) afforded a 9:1 mixture of 1,3-bishomoadamantan-4-one (12) and 5-one (20). The same mixture was also obtained directly from 17 on treatment with diazomethane. The Wolff–Kishner reduction of 12 and 20 gave also 2.

The carbocyclic bishomoadamantane ring system is derivable via ring expansion of homoadamantane or double ring expansion of adamantane and has three possible isomers 1–3. The compound 1, tricyclo[5.3.1.$1^{3,9}$]dodecane or trivial 1,1-bishomoadamantane has been prepared by us[2] previously via the Demjanov–Tiffeneau ring expansion of 4-hydroxy-4-aminomethylhomoadamantane. Compound 3, tricyclo[4.4.1.$1^{3,8}$]dodecane or trivial 1,5-bishomoadamantane has been prepared also by Stepanov,[3] Gerlach,[4] and Majerski[5] via deamination of 1-homoadamantylcarbinylamine or double ring expansion of adamantan-2,6-dione. However, compound 2, tricyclo[4.4.1.$1^{3,9}$]dodecane, 1,3-bishomoadamantane could not be obtained by the solvolytic ring expansion of 3-homoadamantylcarbinyl tosylate (4) because of extensive occurrence of ring contraction on halogenation of the hydrolysis product 5; reduction of the crude bromide gave 3-methylhomoadamantane as the major product and what was presumed to be 2 as the only minor product.[2] This paper describes synthesis of 1,3-bishomoadamantane (2) via the ring expansion of homoadamant-4-en-2-one (7) and homoadamantan-2-one (17).[6,7]

### RESULTS AND DISCUSSION

On treatment of homoadamant-4-en-2-one (7)[8,9] with potassium cyanide and ammonium carbonate in 50% aqueous ethanol, a cyanohydrin derivative **8a** was obtained in 65% yield. On the other hand, trimethylsilylcyanohydrin derivative **8b** was obtained in 83% yield on treatment of 7 with trimethylsilyl cyanide[10] in the presence of zinc iodide.[11] LAH reduction of **8a** and **8b** afforded 2-aminomethyl-2-hydroxyhomoadamant-4-ene (9) in good yields. The assigned *endo*-stereochemistry of $C_2$–OR (R = H and $SiMe_3$) and hence, *exo*-CN and $-CH_2NH_3^+\ Cl^-$ in **8a**, **8b**, and **9** was based on the vinyl proton NMR signals similar to 2-*endo*-hydroxyhomoadamant-4-ene but different from 2-*exo*-hydroxyhomoadamant-4-ene.[8,9] Deamination of **9** with nitrous acid in acetic acid afforded a 95:5 mixture of **10** and **11**, from which the major product **10** was isolated after chromatography and sublimation as a colorless

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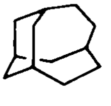

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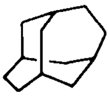

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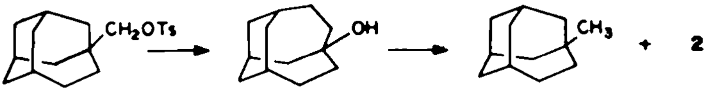


4 5 6

Scheme 1.

solid, m.p. 293–295°, in 84% yield. Appearance of characteristic IR absorption at 1680 cm$^{-1}$ compared to 1710–1712 cm$^{-1}$ for 7[8,9] supported a ring expanded ketone structure of 10. The UV absorption (MeOH) at 225.0 ($\epsilon = 265$) and 296.0 nm (44.5), different from 7 (300 nm, $\epsilon = 127$),[9] indicated the absence of homoconjugation between the CO and olefinic moieties, suggesting a 4-one rather than 5-one structure for 10. The PMR (CDCl$_3$) spectrum revealed signals at δ 6.15–5.45 (m, 2H), 3.4–2.25 (m, 6H) and 2.25–1.2 (m, 8H), which were better resolved with the aid of a shift reagent, tris(dipivalomethanato)-europium(III), and the shift gradient G values[12] were calculated for $H_3$ (16.8), $H_{5a}$ (13.5), $H_{5x}$ (12.2), $H_7$ and $H_8$ (4.2 and 4.3). The similar *G* values for vinyl protons $H_7$ and $H_8$ and the coupling constants for $H_{5x}$ and $H_{5a}$ ($J_{5x,5a} = 14$ Hz, $J_{5x,6} = 6$ Hz, $J_{5a,6} = 1.5$ Hz) supported the assigned 4-one structure for 10 (Scheme 2).

Catalytic hydrogenation (Pd–C) of 10 afforded the corresponding saturated ketone 12 which on sodium borohydride reduction gave 4-hydroxy-1,3-bishomoadamantane (13). The dehydration of 13 with hexamethylphosphoramide (HMPA)[13] or phosphoryl chloride in pyridine afoorded 1,3-bishomoadamant-4-ene (14) in 74 and 83% yields. Compound 14 had IR (KBr) absorptions at 3010 and 1650 cm$^{-1}$ and PMR (CDCl$_3$) signals at δ 6.2–5.35 (m, 2H) and 3.0–1.1 (m, 16H). Catalytic hydrogenation of 14 in methanol (Pd–C) afforded 1,3-bishomoadamantane (2) quantitatively as a colorless solid, m.p. 292–295°, which had correct mass spectral molecular weight (*m/e* 164, M$^+$) and CH analysis. The carbon skeleton structure of 2 was supported by the CMR spectrum (CDCl$_3$) which revealed only eight lines due to the symmetry plane through $C_1$, $C_{11}$, $C_6$ and $C_{12}$ at δ 44.61 (t, 1C), 40.97 (t, 1C), 36.60 (d, 1C), 34.32 (t, 2C), 32.51 (d, 1C), 31.75 (t, 2C), 31.04 (t, 2C), and 29.53 (d, 2C).

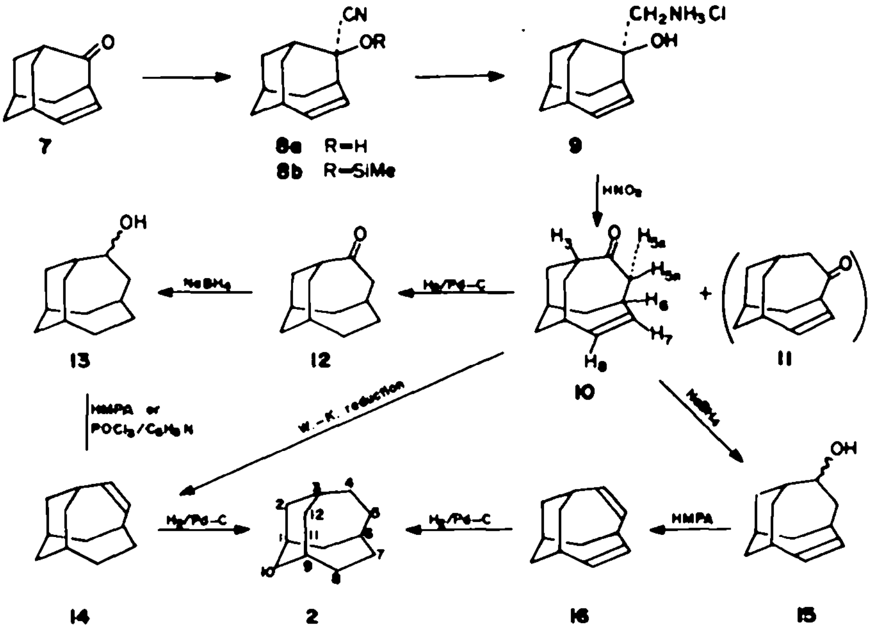
Sodium borohydride reduction of 10 afforded 4-hydroxy-1,3-bishomoadamant-7-ene (15) in 92% yield, which afforded 1,3-bishomoadamanta-4,7-diene (16) on heating in HMPA. The diene structure of 16 was supported by the PMR spectrum which revealed signals at δ 6.25–5.4 (m, 4H) and 3.15–1.1 (m, 12H). Catalytic hydrogenation (Pd–C) of 16 afforded also 1,3-bishomoadamantane (2) quantitatively.

The Wolff–Kishner reduction of 10 afforded also 14. All of these results are summarized in Scheme 2.

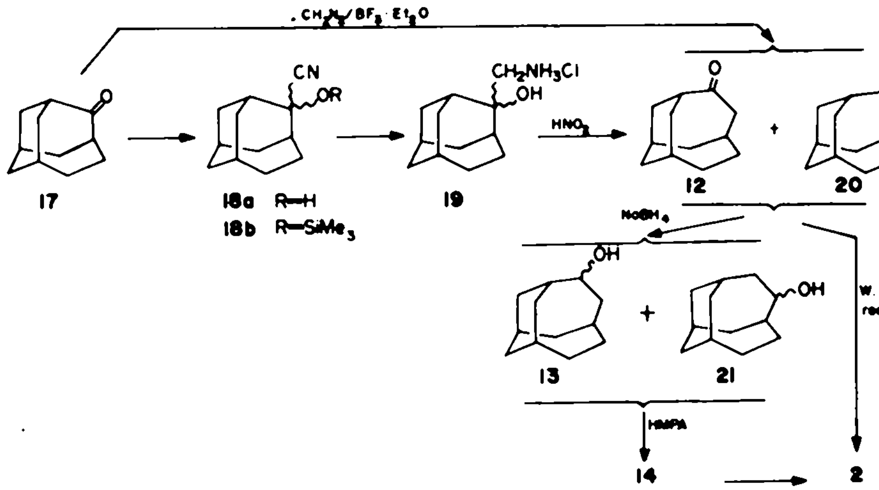
The ring expansion of homoadamantan-2-one (17) was also examined by the Tiffeneu method and diazomethane and the results are summarized in Scheme 3.

The addition of hydrogen cyanide and trimethylsilyl cyanide to 17[8,9] under the conditions described above respectively afforded cyanohydrin derivatives 18a and 18b in 96 and 97% yields. LAH reduction of 18a and 18b gave 2-aminomethyl-2-hydroxy-homoadamantane (19) in good yields, which was characterized as hydrochloride, m.p. 269–272°. Deamination of 19 in aqueous acetic acid with nitrous acid afforded 1,3-bishomoadamantanone in 95% yield. Although this product had IR and PMR spectra superimposable on those of 1,3-bishomoadamantan-4-one (12), and the same retention times as 12 on glc analysis using Silicone SE-30 (2 m) and Apiezon grease L (2 m) columns, it revelaed two peaks in 1:9 ratio on glc analysis using a glass-capillary WCOT column (26 m) coated with QF-1 and DEGS (Experimental); this ring expanded ketone was therefore assigned tentatively as a 9:1 mixture of 12 and 20. Sodium borohydride reduction of the ketone mixture afforded a mixture of the corresponding alcohols 13 and 21 in 69% yield. Dehydration of the alcohol mixture in HMPA afforded a single hydrocarbon which was shown to be identical with 1,3-bishomoadamant-4-ene (14) by comparison of the IR spectrum and glc retention times with those of a sample prepared from 13. Catalytic hydrogenation (Pd–C) of 14 gave 1,3-bishomoadamantane (2) which was also obtained by the Wolff–Kishner reduction of the ketone mixture (12 and 20) as shown in Scheme 3.

Because diazomethane ring expansion of adamantanone is well known to afford homoadamantan-4-one in high yield,[14] 17 was treated overnight at room tem-



Scheme 2.



Scheme 3.

perature with diazomethane generated *in situ* from Diazald (N-methyl-N-nitroso-*p*-toluenesulfonamide) in aqueous ethanol. However, the ring expanded ketone was produced in only 8% yield. By using boron trifluoride etherate as the catalyst,[15] the yield of the ring expansion was raised up to 50%, but the use of a large excess of diazomethane (*ca*. 90-fold excess) afforded many side products.

Our results described above, as well as those recently reported by Murray,[7] establish unequivocal synthetic routes to 1,3-bishomoadamantane (2), and the chemistry, especially the bridgehead reactivity, of bishomoadamantanes 1-3[16] might well be future subjects of interest in view of the theoretically predicted enhanced reactivities of these ring systems.[17]

## EXPERIMENTAL

Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. M.ps. were determined in sealed capillary tubes with a Yanagimoto micro-melting point apparatus (hot-stage type) and are uncorrected. IR spectra were obtained with a Jasco IRA-1 spectrometer and UV spectra with a Jasco ORD/UV-5 spectrometer. $^1$H NMR (PMR) spectra were recorded on a Jeol-C-60HL spectrometer, while $^{13}$C NMR (CMR) spectra were recorded on a Jeol-PFT-100 instrument at 15.04 MHz. All NMR chemical shifts are given in parts per million ($\delta$) downfield from $Me_4Si$ as internal standard. Mass spectra were obtained with a Jeol-01SG spectrometer at 75 eV. Glc analyses were performed with a Jeol JGC-20 K gas chromatograph on 1 and 2 m Silicone SE-30 and Apiezone grease L columns. For analysis of the mixture of 1,3-bishomoadamantan-4-one and 5-one, a 26 m × 0.25 mm (i.d.) WCOT glass-capillary column coated with QF-1 and diethyleneglycol succinate (4:1 ratio) was used at 120° on a Shimazu-5A gas chromatograph.

2 - exo - *Cyano* - 2 - endo - *hydroxyhomoadamant* - 4 - *ene* (8a)

A mixture of 7[8,9] (50 mg, 0.31 mmol), KCN (100 mg, 1.54 mmol), and ammonium carbonate (300 mg, 3.13 mmol) in 50% aq. EtOH (10 ml) was stirred at room temp. for 1 day. The mixture was diluted with water (30 ml) and neutralized with 10% HCl and extracted with ether (5 ml × 4). The combined extracts were washed with 5% HCl and 5% $NaHCO_3$ aq. successively and dried ($Na_2SO_4$). Removal of the solvent gave crude 8a, which was recrystallized from petroleum ether (b.p. 60–65°) to afford 8a (38 mg, 65%): m.p. 209–214° dec.; IR (KBr) 3410, 3040, 2920, 2870, 2240, 1640, 1460, 1350, 1190 and 1110 cm$^{-1}$; PMR ($CDCl_3$) $\delta$ 6.7–5.6 (m, 2H), 2.65 (s, 1H), disappeared on deuteration), and 3.3–1.0 (m, 12H). (Found: C, 76.11; H, 7.86; N, 7.57. $C_{12}H_{15}NO$ requires: C, 76.15; H, 7.99; N, 7.40%).

2 - exo - *Cyano* - 2 - endo - *trimethylsilyloxyhomoadamant* - 4 - *ene* (8b)

To an ice-cooled and stirred mixture of 7 (350 mg, 2.15 mmol) and zinc iodide (16 mg, 0.05 mmol) was added trimethylsilyl cyanide[10] (280 mg, 2.82 mmol) dropwise and the mixture was stirred overnight at room temp. The crude product was purified on a silica gel column eluting with n-hexane to afford 8b as a colorless oil (470 mg, 83.3%): $n_D^{25}$ 1.4934; IR (film) 3040, 2910, 2860, 2240, 1660, 1465, 1455, 1260 and 1140 cm$^{-1}$; PMR ($CDCl_3$) $\delta$ 6.4–5.4 (m, 2H), 3.0–1.15 (m, 12H) and 0.25 (s, 9H).

2 - exo - *Aminomethyl* - 2 - endo - *hydroxyhomoadamant* - 4 - *ene hydrochloride* (9)

A mixture of 8b (425 mg, 1.63 mmol) and LAH (1.8 g, 47 mmol) in ether (70 ml) was heated under reflux for 2 hr. The excess hydride reagent was decomposed under ice-cooling by addition of water and the mixture was extracted with ether (10 ml × 4). The combined extracts were dried ($Na_2SO_4$) and saturated with HCl gas to afford ppts which were recrystallized from MeOH–ether to give 9 as colorless crystals (275 mg, 73.6%): m.p. 289–292°; IR (KBr) 3400–2500 (broad), 1585, 1480, 1140 and 1020 cm$^{-1}$; PMR ($D_2O$) $\delta$ 6.28 (d, d, $J$ = 10.5 and 8.0 Hz, 1H), 5.73 (d, d, $J$ = 10.5 and 8.0 Hz, 1H), 3.25 (s, 2H) and 2.6–1.3 (m, 12H). (Found: C, 62.65; H, 8.96; N, 5.98. $C_{12}H_{20}NOCl$ requires: C, 62.73; H, 8.77; N, 6.10%).

The reduction of 8a with LAH under the similar conditions gave also 9 in 55% yield.

1,3 - *Bishomoadamant* - 7 - *en* - 4 - *one* (*tricyclo*[4.4.1.1$^{3,9}$] - *dodeca* - 7 - *en* - 4 - *one*) (10)

To an ice-cooled and stirred mixture of 9 (200 mg, 0.87 mmol) and NaOAC (120 mg, 1.46 mmol) in AcOH (0.5 ml) and water (1.5 ml) was added dropwise a soln of $NaNO_2$ (150 mg, 2.17 mmol) in water (0.5 ml). After stirring for 0.5 hr, the mixture was warmed at 40° for 0.5 hr and diluted with water to afford colorless ppts which were collected by filtration and washed with water to afford crude ring expanded ketone (140 mg, 91%). Glc analysis revealed two peaks in *ca* 95:5 ratio. Chromatorgraphy on a silica gel column (n-hexane-$CH_2Cl_2$) and sublimation (100°, 20 mm) afforded 10 as a colorless solid (130 mg, 84.7%): m.p. 293–295°; IR (KBr) 3020, 2920, 2860, 1680, 1650 and 1445 cm$^{-1}$; PMR ($CDCl_3$) $\delta$ 6.15–5.45 (m, 2H), 3.4–2.25 (m, 6H), and 2.25–1.2 (m, 8H); UV $\lambda_{max}$ (MeOH) 225.0 ($\epsilon$ = 265) and 296.0 nm (44.5); mass spectrum *m/e* 176 (100, M$^+$), 149 (14), 133 (30), 119 (18), 105 (30), 94 (75), 91 (68), 79 (70) and 77 (42). (Found: C, 81.82; H, 9.10. $C_{12}H_{16}O$ requires: C, 81.77; H, 9.15%).

The minor ketone presumed to be 11 could not be isolated.

1,3 - *Bishomoadamantan* - 4 - *one* (*tricyclo*[4.4.1.1$^{3,9}$]*dodecan* - 4 - *one*) (12)

A mixture of 10 (18 mg, 0.10 mmol) and 10%Pd–C (15 mg) in

MeOH (5 ml) was stirred under an atmospheric pressure of $H_2$ for 5 hr at room temp. Removal of the catalyst through Celite and evaporation of the solvent afforded crude product which was sublimed (95°, 20 mm) to give the saturated ketone 12 (17 mg, 94%): m.p. > 300°; IR (KBr) 1680, 1450 and 1180 $cm^{-1}$; PMR ($CDCl_3$) $\delta$ 2.62 (unsymmetrical d, $J = 4.5$ Hz, 2H) and 3.0–0.8 (m, 16H); mass spectrum *m/e* 178 (100, $M^+$), 108 (91), 93 (52), 79 (80), 67 (73), 55 (46) and 41 (99). (Found: C, 80.88; H, 10.15. $C_{12}H_{18}O$ requires: C, 80.85; H, 10.18%).

### 1,3 - *Bishomoadamantan* - 4 - *ol* (*tricyclo*[4.4.1.$1^{3,9}$] - *dodecan* - 4 - *ol*) (13)

The ketone 12 (150 mg, 0.84 mmol) and $NaBH_4$ (180 mg, 4.75 mmol) in MeOH (15 ml) was stirred under ice-cooling for 1 hr and at room temp. for 3 hr. The diluted mixture was saturated with NaCl and extracted with ether (10 ml × 8) and the combined extracts were dried ($Na_2SO_4$). Removal of the solvent afforded crude alcohol which was purified by sublimation (95°, 20 mm) and recrystallization from n-pentane to give 13 as colorless crystals (115 mg, 76%): m.p. > 300°; IR (KBr) 3320, 2910, 2700, 1470 and 1020 $cm^{-1}$; PMR ($CDCl_3$) $\delta$ 4.2–3.5 (m, 1H), 2.6–1.0 (m, 18H), and 1.36 (s, *ca* 1H, disappeared on shaking with $D_2O$); mass spectrum *m/e* 180 (4.5%, $M^+$), 162 (100), 93 (93) and 79 (66). (Found: C, 80.07; H, 11.03. $C_{12}H_{20}O$ requires: C, 79.94; H, 11.18%).

### 1,3 - *Bishomoadamant* - 4 - *ene* (*tricyclo*[4.4.1.$1^{3,9}$]*dodeca* - 4 - *ene*) (14)

(A) The alcohol 13 (15 mg, 0.083 mmol) was heated under reflux in HMPA (1 ml) under argon atmosphere for 4 hr. The cooled mixture was diluted with water (10 ml) and extracted with $CH_2Cl_2$ (5 ml × 4). The combined extracts were washed with water and dried ($Na_2SO_4$). Removal of the solvent gave crude product which was purified on a short silica gel column eluting with n-pentane and sublimed (80°, 30 mm) to afford 14 as a colorless solid (10 mg, 74%): m.p. 265–268°; IR (KBr) 3010, 2895, 2840, 1650 and 1445 $cm^{-1}$; PMR ($CDCl_3$) $\delta$ 6.2–5.35 (m, 2H) and 3.1–1.1 (m, 16H); mass spectrum *m/e* 163 (25), 162 (100, $M^+$), 149 (47), 109 (45), 106 (70), 105 (60), 93 (63), 92 (78), 91 (70) and 79 (64). (Found: C, 89.02; H, 10.97. $C_{12}H_{18}$ requires: C, 88.82; H, 11.18%).

(B) To a stirred and ice-cooled soln of 11 (20 mg, 0.11 mmol) in anhyd. pyridine (2 ml) was added $POCl_3$ (1 ml) dropwise and the mixture was stirred for a further 15 hr at room temp. The mixture was poured onto ice-water and extracted with n-pentane (5 ml × 4) and the combined extracts were washed with water and dried ($Na_2SO_4$). Removal of the solvent gave crude product which was purified as above to afford 14 (15 mg, 83%), which was identical with the sample prepared by the method A on IR spectral and glc comparison.

(C) A mixture of 10 (20 mg, 0.11 mmol), 100% hydrazine hydrate (500 mg, 10 mmol), and hydrazine dihydrochloride (50 mg, 0.48 mmol) in diethylene glycol (8 ml) was heated at 110–150° for 2 hr. The mixture was cooled and KOH (280 mg) was added. The mixture was then heated again allowing distillation of hydrazine hydrate, and the heating was continued for 4 hr at 220–230°. The cooled mixture was diluted with water and extracted with n-pentane (5 ml × 3). The distilate was also extracted with n-pentane after dilution and the distilling head was washed with n-pentane. The combined extracts and washings were washed with water and dried ($Na_2SO_4$). Removal of the solvent gave crude product which was purified as above to give the olefin 14 (10 mg, 56%).

### 1,3 - *Bishomoadamant* - 7 - *en* - 4 - *ol* (*tricyclo*[4.4.1.$1^{3,9}$]*dodeca* - 7 - *en* - 4 - *ol*) (15)

A mixture of 10 (70 mg, 0.40 mmol) and $NaBH_4$ (105 mg, in MeOH (7 ml) was stirred for 0.5 hr under ice-cooling and for 2 hr at room temp. Work-up as above and chromatography on a silica gel column eluting with $CH_2Cl_2$–n-hexane and sublimation (95°, 18 mm) afforded the alcohol 15 as colorless crystals (65 mg, 91.8%): m.p. > 300°; IR (KBr) 3440, 1645, 1445, 1410 and 1015 $cm^{-1}$; PMR ($CDCl_3$) $\delta$ 6.3–5.6 (m, 2H), 4.45–3.7 (broad s, 1H), 2.9–1.1 (m, 14H) and 2.27 (s, 1H, disappeared on deuteration); mass spectrum *m/e* 179 (13), 178 (56, $M^+$), 160 (16), 91 (69), 79 (66), 44 (100), and 41 (94). (Found: C, 80.58; H, 10.22. $C_{12}H_{18}O$ requires: C, 80.85; H, 10.18%).

### 1,3 - *Bishomoadamanta* - 4,7 - *diene* (*tricyclo*[4.4.1.$1^{3,9}$]*dodeca*-4,7-*diene*) (16)

The alcohol 15 (20 mg, 0.11 mmol) was heated under reflux in HMPA (1 ml) under argon atmosphere for 4 hr. The cooled mixture was then diluted with water and worked up with n-pentane to give 16 as colorless crystals after sublimation (15 mg, 83.4%); m.p. 220–223°; IR (KBr) 3010, 2905, 2840, 1650 and 1440 $cm^{-1}$; PMR ($CDCl_3$) $\delta$ 6.25–5.4 (m, 4H) and 3.15–1.1 (m, 12H); mass spectrum *m/e* 161 (4.3), 160 (60, $M^+$), 131 (24), 117 (44), 91 (92) and 79 (100). (Found: C, 90.17; H, 9.83. $C_{12}H_{16}$ requires: C, 89.94; H, 10.06%).

### 2 - *Cyano* - 2 - *hydroxyhomoadamantane* (18a)

A mixture of 17[4,9] (70 mg, 0.43 mmol), KCN (100 mg, 1.54 mmol) and $(NH_4)_2CO_3$ (300 mg, 3.13 mmol) in 50% aqueous EtOH (10 ml) was stirred for 1 day at room temp. The mixture was diluted with water (30 ml) and extracted with $CH_2Cl_2$ (10 ml × 4). The combined extracts were washed successively water, 5% HCl. 5% $NaHCO_3$aq and water and dried ($Na_2SO_4$). Removal of the solvent afforded crude product which was recrystallized from petroleum ether (b.p. 60–65°) to give 18a as colorless crystals (78 mg, 95.7%): m.p. 238–241° (dec); IR (KBr) 3400, 2900, 2240, 1450, 1350 and 1060 $cm^{-1}$; PMR ($CDCl_3$) $\delta$ 3.0 (broad s, 1H, disappeared on deuteration), and 2.7–0.2 (m, 16H). (Found: C, 75.18; H, 8.84; N, 7.32. $C_{12}H_{17}NO$ requires: C, 75.35; H, 8.96; N, 7.32%).

### 2 - *Cyano* - 2 - *trimethylsilyloxyhomoadamantane* (18b)

To a stirred mixture of 17 (250 mg, 1.52 mmol) and zinc iodide (5 mg) was added dropwise trimethylsilyl cyanide[10] (200 mg, 2.00 mmol) under ice-cooling and the stirring was continued for 15 hr at room temp. After removal of the excess trimethylsilyl cyanide under reduced pressure, the crude product was purified on a silica gel column eluting with n-hexane to afford 18b as a colorless oil (390 mg, 97%): $n_D^{24}$ 1.4941; IR(film) 2940, 2870, 2240 and 1450 $cm^{-1}$.

### 2 - *Aminomethyl* - 2 - *hydroxyhomoadamantane hydrochloride* (19)

(A) The cyanohydrin 18a (110 mg, 0.58 mmol) was hydrogenated in the presence of $PtO_2$ (5 mg) in EtOH (1.5 ml) containing conc HCl (0.05 ml) under an atmospheric pressure of $H_2$ for 15 hr at room temp. Removal of the solvent after filtration through Celite gave crude product which was recrystallized from MeOH–$Et_2O$ to give 19 as colorless crystals (115 mg, 85.5%): m.p. 269–272°; IR (KBr) 3380, 3020, 2910, 1595, 1495 and 1450 $cm^{-1}$; PMR ($D_2O$) $\delta$ 3.19 (s, 2H) and 2.55–1.1 (m, 16H). (Found: C, 62.48; H, 9.49; N, 6.19. $C_{12}H_{22}NOCl$ requires: C, 62.19; H, 9.57; N, 6.04%).

Reduction of 18a (510 mg, 2.66 mmol) with LAH (2.0 g, 53 mmol) in refluxing either for 18 hr and usual work-up also afforded 19 (228 mg, 37%).

(B) A mixture of 18b (800 mg, 3.04 mmol) and LAH (2.0 g, 53 mmol) in ether (30 ml) was heated under reflux for 3 hr. The usual work-up and extraction with ether, followed by treatment with HCl gas afforded crude 19 which was reprecipitated from MeOH–$Et_2O$ (620 mg, 74.5%).

### 1,3 - *Bishomoadamantan* - 4 - *one* (12) *and* - 5 - *one* (20)

(A) To an ice-cooled and stirred soln of 19 (590 mg, 2.54 mmol) and NaOAc (450 mg, 5.48 mmol) in water (4.5 ml) and AcOH (1.5 ml) was added $NaNO_2$aq (450 mg, 6.52 mmol) dropwise during 0.5 hr and the stirring was continued for 2 hr at 30–40°. Dilution of the mixture with water afforded a ppt which was filtered off and washed with water. The filtrate and washings were combined and neutralized with 10% NaOHaq and extracted with $CH_2Cl_2$ (10 ml × 2). The combined extracts were washed with water and dried ($Na_2SO_4$). Removal of the solvent gave a second crop of the ring expanded ketone, which was combined with the ppt and sublimed (95°, 1 mm) to afford a 90:10 mixture of 12 and 20 (430 mg, 94.8%), m.p. > 300°. The IR (KBr and PMR ($CDCl_3$) spectra were superimposable on those of 12.

(B) To an ice-cooled and stirred mixture of 17 (5 mg, 0.03 mmol) and Diazald (0.2 g, 0.9 mmol) in 95% EtOH (0.3 ml) was added KOH in 50% aq EtOH (0.7 ml) and the mixture was stirred overnight at room temp. The diluted mixture was extracted with ether (5 ml × 3) and the combined extracts were washed with either and dried ($Na_2SO_4$). Removal of the solvent and sublimation gave a mixture of 17 and the ring expanded ketone (12 + 20) in 92:8 ratio (3 mg).

To an ice-cooled and stirred mixture of 17 (5 mg, 0.03 mmol) and $BF_3$ etherate (10 mg) in ether (1 ml) was added diazomethane (*ca* 0.3 mmol) in ether (3 ml). After being stirred overnight at room temp, the mixture was washed with water, dried ($Na_2SO_4$), and the solvent was removed to give crude product (5 mg), which contained *ca* 50% of the bishomoadamantanone (12 + 20).

### 1,3 - *Bishomoadamantan* - 4 - *ol* (13) *and* - 5 - *ol* (21)

The ketone mixture (12 and 20) (50 mg, 0.28 mmol) was reduced with $NaBH_4$ (60 mg, 1.58 mmol) in MeOH (7 ml) for 5 hr at room temp. The mixture was diluted with NaClaq and extracted with ether (5 ml × 6). The combined extracts were dried ($Na_2SO_4$) and evaporated to give crude alcohol which was recrystallized from n-pentane to afford 13 and 21 (35 mg, 69.2%), m.p. > 300°. The IR and PMR spectra were the same as those of 13, and the dehydration on heating in HMPA gave 1,3-bishomoadamantene (14).

### 1,3 - *Bishomoadamantane* (*tricyclo*[4.4.1.1$^{3,9}$]*dodecane*) (2)

(A) Compound 14 (30 mg, 0.18 mmol) was hydrogenated in the presence of Pd–C (10%, 5 mg) in MeOH (2 ml) for 10 hr under an atmospheric pressure of $H_2$ at 20–25°. The catalyst was removed by filtration and the filtrate was diluted with water and extracted with n-pentane (5 ml × 3). The combined extracts were dried ($Na_2SO_4$) and evaporated carefully to give crude product which was sublimed (90°, 100 mm) to afford 2 as a colorless solid (30 mg, 98.8%): m.p. 292–295°; IR (KBr) 2900, 2700, 1455, 1170, 1110 and 808 $cm^{-1}$; PMR ($CDCl_3$) $\delta$ 2.6–0.8 (m); CMR see Text; mass spectrum *m/e* 165 (20), 164 (100, $M^+$), 135 (35), 121 (26), 107 (42) and 93 (58). (Found: C, 87.90; H, 12.10. $C_{12}H_{20}$ requires: C, 87.73; H, 12.27%).

(B) The diene 16 also gave 2 quantitatively on hydrogenation in the presence of 10%Pd–C in MeOH.

(C) The Wolff-Kishner reduction of the ketone mixture (30 mg, 0.18 mmol) under the conditions described above for 10 also afforded 2 (8 mg, 27%) after usual work-up and sublimation (80°, 30 mm).

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