Hydride Transfer Reduction–Rearrangement of 2,4-Dehydro-4-homotwistane. Detection and Identification of 2,4-Bishomobrendane

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Received October 26, 1976

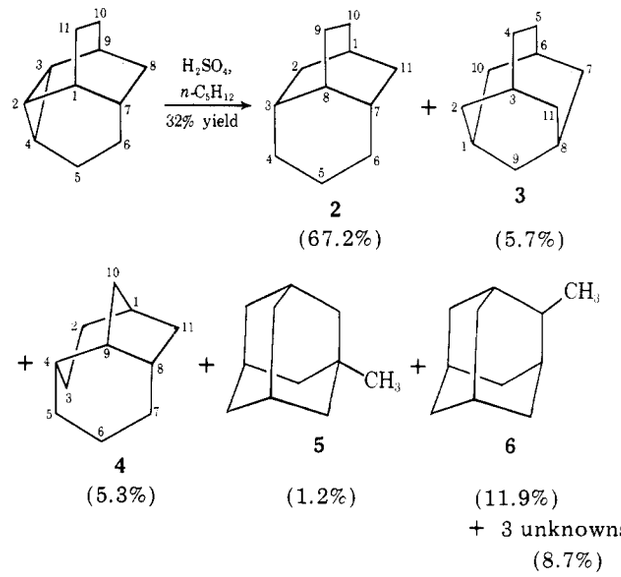
Treatment of 2,4-dehydro-4-homotwistane (1) with sulfuric acid–*n*-pentane at room temperature resulted in protonation with rupture of the cyclopropane ring, partly accompanied by skeletal rearrangement. Besides 4-homoisotwistane (2), homoadamantane (3), and 1- and 2-methyladamantane (5 and 6) was obtained a new tricycloundecane as one of the products, which was identified as 2,4-bishomobrendane (4) by comparison of GC/MS behavior with that of an independently synthesized authentic specimen. The predominant isomerization product from 4-homoisotwistan-*exo*-2-ol (18) was 4, suggesting that the formation of 4 from 1 was preceded by 4-homoisotwist-2-yl cation (2c), one of the protonation products of 1. Other protonation products, *endo*-3,7-ethanobicyclo[3.2.2]nonyl cations (19a and 19b), were considered to lead to methyladamantanes (5 and 6) via homoadamantyl cations (3a and 3b).

2,4-Dehydro-4-homotwistane (tetracyclo[5.4.0.0^{2,4}.0^{3,9}]-undecane, 1) has been prepared by Krantz and Lin.[1] It seems quite intriguing to study protonation with rupture of the cyclopropane ring[2] in the tetracyclic compound 1, because the reaction, if it occurs, leads to the formation of a variety of cationic species possibly involved in the adamantane rearrangement of tricycloundecanes. For example, protonation at C-3 followed by rupture of the bond between C-3 and C-4 gives rise to 4-homoisotwist-4-yl cation (2b; path c, Scheme IV), which was assumed to be the progenitor of intermediates arising in the transformation of 4-homoisotwistane (tricyclo[5.3.1.0^{3,8}]undecane, 2) into final rearrangement products, methyladamantanes.[3a] Two cations[4,5] (19a and 19b; paths a and d) have the skeleton of a protohomoadamantane which was shown[3a,6,7] to be directly related to homoadamantane (3).

Under the reaction conditions of hydride transfer reduction–rearrangement[8] (i.e., in the presence of some hydride source coupled with acid catalyst), these ions may isomerize further to give various tricycloundecane isomers. These isomerization processes, therefore, correspond to local pathways of the tricycloundecane rearrangement. Thus study of the hydride transfer reduction–rearrangement of 1 should contribute to the elucidation of the role of postulated cations in hitherto unclarified[3] isomerization sequence from 4-homoisotwistane to methyladamantanes.

Reaction of 2,4-Dehydro-4-homotwistane (1) with Sulfuric Acid–*n*-Pentane. Concentrated (95%) sulfuric acid[2a] was found to effect rupture of the cyclopropane ring in 2,4-dehydro-4-homotwistane (1). In a reaction in the presence of *n*-pentane[2a] at ambient temperature for 30 min, products (32% combined yield) detected and identified on Golay GC/MS were 4-homoisotwistane (2), homoadamantane (3), methyladamantanes (5 and 6), and a new tricycloundecane of as yet unknown structure (Scheme I). This tricycloundecane was determined to be 2,4-bishomobrendane (tricyclo[6.2.1.0^{4,9}]undecane, 4) by comparison of GC/MS behavior with that of an independently synthesized authentic specimen, as described below.

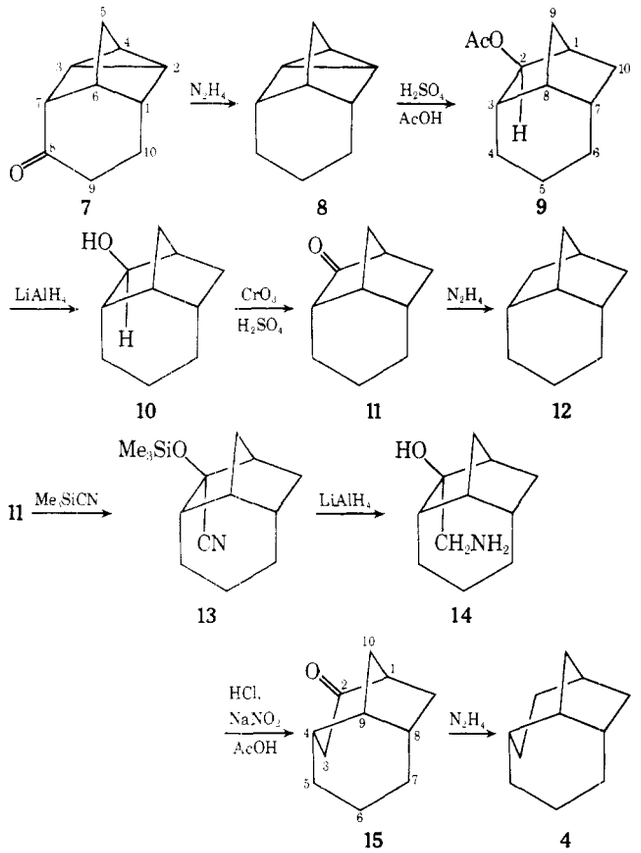
Scheme I



2,4-Bishomobrendane (4). Synthesis of 2,4-bishomobrendane (4) is a problem that has been with us since the early stage of our study on tricycloundecane rearrangements. This unknown hydrocarbon is considered to play an important role in local rearrangement pathways in which 4-homoisotwistane takes part. For example, acid-catalyzed isomerization of 4-homoisotwistane (2) gave a quasi-equilibrium mixture consisting of a number of tricycloundecane isomers such as 1,*exo*-2-trimethylene-*cis*-bicyclo[3.3.0]octane, 1,*exo*-2-tetramethylenenorbornane, 1,2-trimethylenebicyclo[2.2.2]-octane, [3.3.3]propellane, and homoadamantane (3).[3a] 2,4-Bishomobrendane (4) was postulated on the mechanistic basis as an intermediate in going from 2 to some of these equilibrating isomers.[3a]

A tricycloundecane denoted as unknown D has been detected in various phases of tricycloundecane rearrangement.[3] For example, unknown D was formed whenever 4-homoisotwistane (2) was produced in the rearrangement. Isomerization of 2 itself afforded unknown D already at the beginning of the reaction. It was also one of the major intermediates in the isomerization of *cis*-2,3-trimethylenebicyclo[2.2.2]octane to 2. These results indicate a close relationship between 2 and unknown D, and probably only a few steps would be involved in their mutual interconversion. Unknown D was recently identified by us[9] as *endo*-2,8-trimethylene-*cis*-bicyclo[3.3.0]-octane (tricyclo[5.3.1.0^{4,11}]undecane, 16, Chart I). It then seems most reasonable to assume 2,4-bishomobrendane (4) as the intermediate of the interconversion between 2 and 16, in view of the established equilibrium among bicyclo[2.2.2]-, -[3.2.1]-, and -[3.3.0]octane.[10] Indeed three tricycloundecanes 2, 4, and 16 are trimethylene derivatives of these bicyclooctanes. In order to examine the above postulate on the role of 2,4-bishomobrendane (4) in tricycloundecane rearrangement, an authentic specimen of 4 was prepared according to Scheme II.

Scheme II



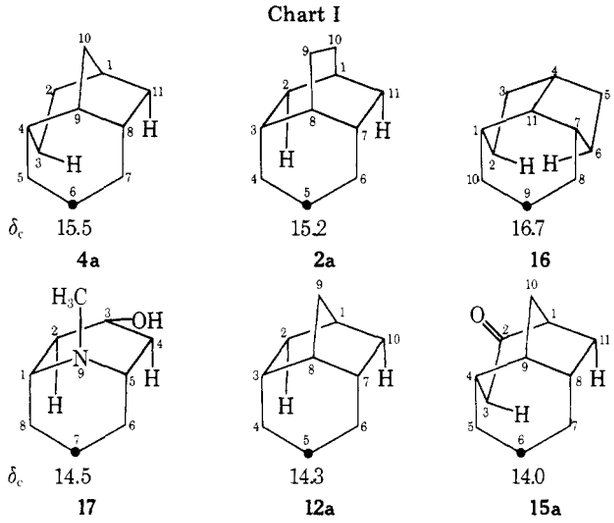
Synthesis of 2,4-bishomobrendane (**4**) started with 2,10-dehydro-4-homobrendan-4-one (tetracyclo[4.4.0.0^{2,4}.0^{3,7}]-decan-8-one, **7**).[11] The ketone **7** was obtained from 2,9-dehydro-4-cyanobrendane, the Diels–Alder adduct of acrylonitrile with homoconjugated norbornadiene in the presence of bisacrylonitrile nickel,[12] by reduction, Demjanow rearrangement, and subsequent chromic acid oxidation.[11] Wolff–Kishner reduction of **7** afforded the corresponding hydrocarbon, 2,10-dehydro-4-homobrendane (tetracyclo[4.4.0.0^{2,4}.0^{3,7}]decane, **8**). The hydrocarbon **8** was found to undergo addition of acetic acid in the presence of sulfuric acid with rupture of the cyclopropane ring,[2b] giving almost exclusively the *exo*-2-acetoxy derivative (**9**)[13] of 4-homobrendane (tricyclo[5.2.1.0^{3,8}]decane, **12**).[14] Lithium aluminum hydride reduction of **9** gave 4-homobrendan-*exo*-2-ol (**10**), which had the same melting point as that described by Spurlock for the compound.[13] The carbinol **10** was converted by Jones oxidation to 4-homobrendan-2-one (**11**), which also had the same melting point as that of an authentic specimen.[13] The ketone **11** was reduced by hydrazine to the hydrocarbon, 4-homobrendane (**12**),[14] which showed a ^{13}C NMR spectrum comprising seven signals with correct relative intensity and splitting on off-resonance proton decoupling corresponding to the structure.

Reaction of the ketone **11** with trimethylsilyl cyanide[15] led to the formation[16] of the trimethylsilyl ether (**13**) of the cyanohydrin of **11**, which was reduced by lithium aluminum hydride[16] to the corresponding amino alcohol (**14**). Tiffeneau–Demjanow rearrangement of **14** gave almost exclusively an isomer of bishomobrendanone. This result may indicate that the isomer obtained is most probably the 2-one (**15**) and, at the same time, that the amino alcohol **14** has the configuration of the *endo*-2-aminomethyl-*exo*-2-hydroxy isomer. This inference is made from the product distribution in the same reaction of the two configurational isomers of 2-aminomethyl-2-hydroxynorbornane,[17] assuming a similar stereoelectronic requirement for both compounds. Wolff–Kishner reduction of **15** afforded the final product, 2,4-bishomobrendane (**4**).

The VPC retention time and mass spectrum of an authentic specimen of **4** thus prepared were incidentally compared with those of the unknown formed in the hydride transfer reduction–rearrangement of 2,4-dehydro-4-homotwistane (**1**). It happened that these properties completely agreed with each other.

^{13}C NMR Spectrum of 2,4-Bishomobrendane (4). The ^{13}C NMR spectrum of 2,4-bishomobrendane (**4**) contained a single intensity triplet signal at an abnormally high field (15.5 ppm), as compared to those of ordinary methylene groups. This upfield shift can be attributed to steric compression exerted on a chair form cyclohexane carbon atom (C-6 in **4a**, Chart I) by two endo hydrogens on 3,5-diaxial methylene

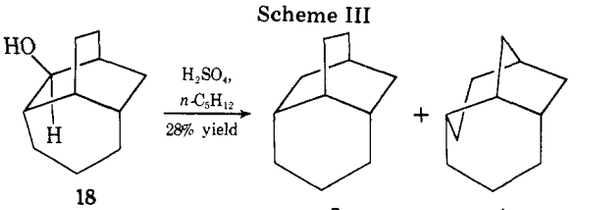
Chart I



substituents (C-3 and C-11). Some precedents for this type of steric compression in bridged compounds have been found for 4-homoisotwistane (**2a**, C-5),[3b] *endo*-2,8-trimethylene-*cis*-bicyclo[3.3.0]octane (**16**, C-9),[9] and *endo*-3-hydroxy-9-methyl-9-aza-(*Z*)-bicyclo[3.3.1]nonane (**17**, C-7).[18] The same effect was observed also for 2,4-bishomobrendan-2-one (**15a**, C-6) as well as for 4-homobrendane (**12a**, C-5) prepared above (Scheme II).

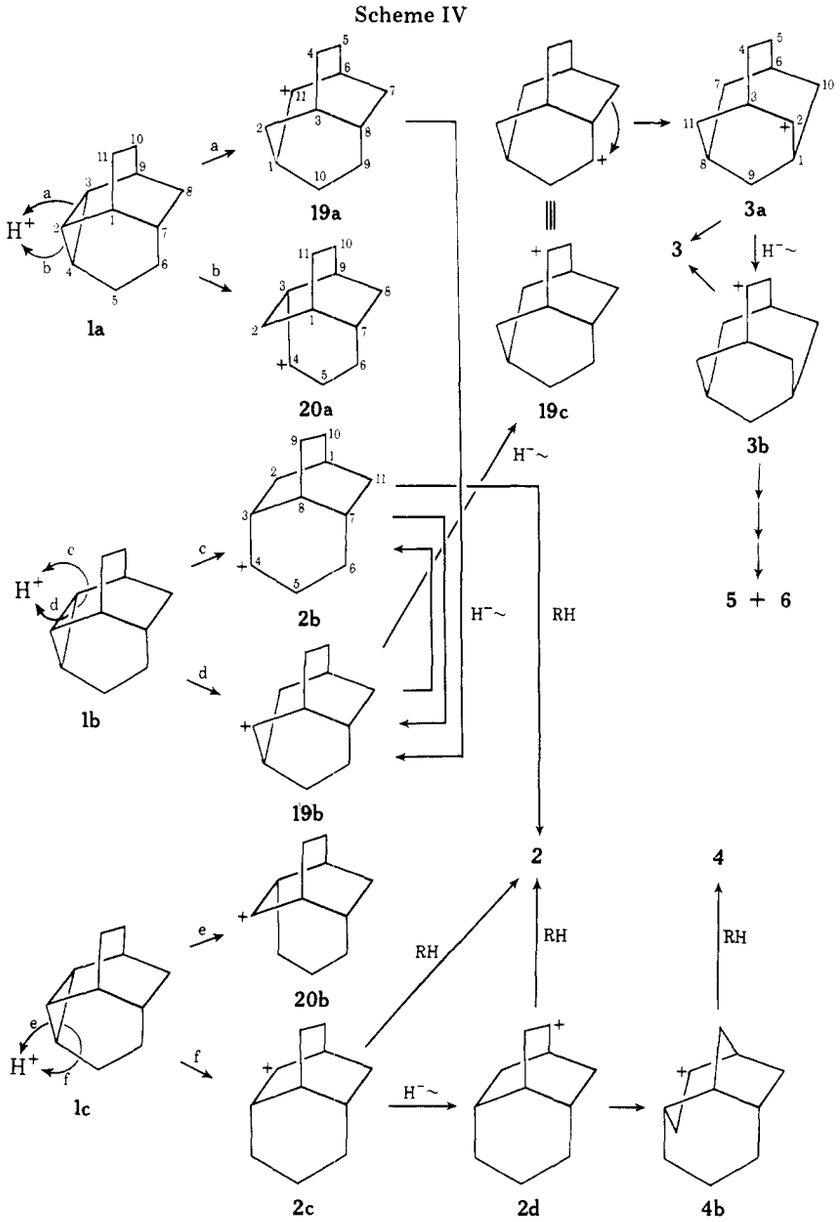
Hydride Transfer Reduction–Rearrangement of *exo*-2-Hydroxy-4-homoisotwistane (18). There is a possibility for 4-homoisotwist-2-yl cation (**2c**, Scheme IV) to be formed from 2,4-dehydro-4-homotwistane (**1**) according to path f. In order to see the fate of this cation in the reaction, **2c** was generated from *exo*-2-hydroxy-4-homoisotwistane (**18**)[19] by treatment with sulfuric acid in the presence of *n*-pentane, and the reaction was run for 5 min. The result is shown in Scheme III.

Scheme III



The major product of the reaction was 4-homoisotwistane (**2**), product of the simple hydride transfer reduction, and only less than 30% of the reactant was isomerized. The predomi-

Scheme IV



nant isomerization product was 2,4-bishomobrendane (**4**), neither homoadamantane (**3**) nor methyladamantanes (**5** and **6**) being detected at all. Three unknowns (*m/e* 150) were the same compounds as those found in the reaction of **1** (Scheme I), as identified on Golay GC/MS.

Discussion

There exist formally six possibilities (**19a, 20a, 2b, 19b, 20b,** and **2c**) for the formation of tricycloundecyl cations from 2,4-dehydro-4-homotwistane (**1**), according to the position of protonation (giving the cations **1a–c**) and the location of the bond to be cleaved (paths a–f) (Scheme IV). These transformations give three different tricycloundecane structures, 4-homoisotwistane (**2**), *endo*-3,7-ethanobicyclo[3.2.2]nonane (tricyclo[4.4.1.0^{3,8}]undecane, **19**),[5] and 4-homotwistane (tricyclo[5.4.0.0^{3,9}]undecane, **20**).

It seems reasonable from the reaction of 4-homoisotwistan-*exo*-2-ol (**18,** Scheme III) to explain the formation of 2,4-bishomobrendane (**4**) in terms of the cation **2c** (path f). The pathway to **4** involves hydride transfer in **2c** to give **2d,** that would most probably be a 1,3-intramolecular process. Final step of the pathway is conversion of **2d** into **4b,** which is a similar process to isomerization of bicyclo[2.2.2]octyl to bicyclo[3.2.1]octyl system.[10]

A close relationship between homoadamantane (**3**) and *endo*-3,7-ethanobicyclo[3.2.2]nonane (**19**) in carbonium ion rearrangements has been well demonstrated. Diacetoxy derivatives of **19** were obtained by silver ion catalyzed bromination–solvolysis of 2,4-dehydrohomoadamantane.[6] Formation of 4-homoisotwistane (**2**) from 4-homoadamantanol[7] as well as from 2-homoadamantanol[20] in sulfuric acid was most plausibly explained by the intermediacy of the cation **19c.** Therefore, 2-homoadamantyl cation (**3a**), and hence homoadamantane (**3**), is apparently formed from **19c** (Scheme IV). The cation **19c,** in turn, is considered to be derived from **19b** by intramolecular 1,3-hydride transfer, and no detection (Scheme I) of the hydrocarbon **19,** in spite of its being a fairly stable compound[21] (see below), should be attributed to the intramolecular nature of this process. In contrast, the cation **19a** cannot be a direct precursor to **19c** because the conversion must be a bimolecular process (intermolecular 1,4-hydride transfer). Therefore any **19a** must be transformed into **19b** by 1,3-intramolecular hydride transfer before it isomerizes to the homoadamantane structure.

Postulated intermediacy of the cation **19c** in the isomerization of homoadamantane (**3**) to 4-homoisotwistane (**2**)[7,20] suggests that a part of the cation **19b** may isomerize to 4-homoisotwist-4-yl cation (**2b**). Conversely, the cation **2b** may

follow the reverse reaction sequence to give the homoadamantane structure: **2b** to **19b** to **19c** to **3a**. In contrast to rather facile interconversion between **19a** and **19b** as well as that between **19b** and **19c**, hydride transfer in the 4-homoisotwist-2-yl cation (**2c**) to give the 4-yl cation (**2b**) seems to be unfavorable, although it is seemingly a 1,3-intramolecular process. This is inferred from the result that the reaction of the cation **2c** (Scheme III) does not give rise to any isomerization products expected from the 4-yl cation **2b** (**3, 5,** and **6**). This inhibition of the intramolecular 1,3-hydride transfer in **2c** should arise from an unfavorable transposition of the vacant p orbital on the cationic carbon atom and the σ orbital of the hydride (endo-4-H) to be shifted, the relevant orbitals being almost perpendicular with each other.

It has been established that 2-homoadamantyl (**3a**)[20] and 4-homoadamantyl (**3b**)[7] cations are partly transformed in sulfuric acid–*n*-pentane into methyladamantanes. Predominance of 2-methyladamantane (**6**) over the 1-methyl isomer (**5**) is noted in these reactions. Indeed **6** was the only methyladamantane formed from 2-homoadamantanol.[20] Majerski[7] demonstrated by the use of ^{13}C-enriched 4-homoadamantanol that ring contraction in the 4-homoadamantyl cation (**3b**) gave **6** directly. On the basis of these results, predominance of **6** in the reaction of 2-homoadamantanol was interpreted[20] by the intermediacy of the 4-homoadamantyl cation (**3b**) which was formed from the 2-yl cation **3a** by 1,3-intramolecular hydride transfer. In the present reaction was also found predominance of **6** over **5** (10:1). This result is consistent with Scheme IV in which 4-homoadamantyl cation **3b** is regarded as the major precursor to methyladamantanes. There seems to be little possibility for the formation of methyladamantanes from once-formed neutral 4-homoisotwistane (**2**), because **2** isomerizes quite sluggishly under sulfuric acid catalysis.[3b]

The remaining possibilities for the cyclopropane ring cleavage in 2,4-dehydro-4-homotwistane (**1**) are those leading to 4-homotwistane structure (**20**) (paths b and e). No definite conclusion can be drawn from the present experimental results as to whether or not these processes actually occur. This is because the product distribution in the reaction of **1** is well explained with the intermediacy of the cations **2b, 2c, 19a,** and **19b** on one hand, and because nothing has been studied so far about the reaction of 4-homotwistyl cation **20a** and **20b** on the other. However, comparison of the stability of the products in these cyclopropane ring cleavages suggests that paths b and e leading to **20** might be unfavorable as compared to the others giving **2** and **19.** Molecular mechanics calculations[7,21] showed that the calculated heats of formation for the hydrocarbons **2, 19,** and **20** were −30, −27, and −23 kcal/mol, respectively. The 4-homotwistane structure (**20**) is thus the least stable of the three and, therefore, is the least possibly formed from **1,** if the reaction is under thermodynamic control. Indeed thermodynamic control has been shown to prevail in extensive skeletal rearrangement of polycyclic hydrocarbons in the presence of acid catalyst.

Experimental Section

All melting and boiling points are uncorrected. Measurements of IR, ^1H and ^{13}C NMR, and mass spectra as well as conventional VPC and Golay GC/MS measurements were made on the same instruments as in the previous works.[3,8]

2,4-Dehydro-4-homotwistane (**1**),[1] 2,10-dehydro-4-homobrendan-8-one (**7**),[11] and *exo*-2-hydroxy-4-homoisotwistane (**18**)[19] were prepared according to the method of the literature.

2,10-Dehydro-4-homobrendane (8). A mixture of 12 g (0.081 mol) of 2,10-dehydro-4-homobrendan-8-one (**7**), 10 g of potassium hydroxide, 50 mL of 100% hydrazine hydrate, and 80 mL of diethylene glycol was heated with stirring at 140 °C for 2 h. The reaction mixture was then heated at 210 °C for 4 h while water formed was distilled. After being cooled, the reaction mixture was extracted with three 100-mL portions of *n*-hexane. The combined hexane extracts were washed with two 50-mL portions of water and dried over anhydrous sodium sulfate. The solution was concentrated, and the residue was fractionally distilled to give 3.52 g (32% yield) of 2,10-dehydro-4-homobrendane (**8**): bp 72 °C (19 mm); IR (neat) 3050, 2930, 1460, 1440, 1390, 920, 800 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ_C 12.7 (d, 2, C-2, C-3), 12.9 (d, 1, C-4), 18.0 (t, 1, C-9), 26.5 (t, 2, C-8, C-10), 34.2 (t, 1, C-5), 37.9 (d, 1, C-6), 40.2 (d, 2, C-1, C-7); mass spectrum *m/e* (rel intensity) 134 (91, M^+), 119 (42), 106 (31), 105 (39), 93 (31), 92 (58), 91 (100), 80 (70), 79 (57), 66 (49).

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.6; H, 10.3.

***exo*-2-Acetoxy-4-homobrendane (9).** A solution of 2.76 g (0.021 mol) of 2,10-dehydro-4-homobrendane (**8**) and 1 mL of 95% sulfuric acid in 120 mL of glacial acetic acid was heated at 100 °C for 1.5 h. The reaction mixture was cooled, diluted with 50 mL of water, and extracted with five 50-mL portions of petroleum ether. The combined extracts were washed with water, dried over anhydrous sodium sulfate, and concentrated. The residue was fractionally distilled to give 3.11 g (78% yield) of *exo*-2-acetoxy-4-homobrendane (**9**) which was found homogeneous on conventional VPC: bp 124 °C (15 mm); IR (neat) 2950, 1740, 1250, 1020 cm^{-1}; mass spectrum *m/e* (rel intensity) 134 (100), 119 (17), 92 (20), 91 (19), 81 (17), 80 (55), 79 (17), 67 (14), 43 (70), 41 (16).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.4; H, 9.4.

An exo configuration of the acetoxy group in **9** is apparent from that of the corresponding alcohol **10**[12] derived from it, as described in the following paragraph.

***exo*-2-Hydroxy-4-homobrendane (10).** To a stirred suspension of 1 g (0.026 mol) of lithium aluminum hydride in 10 mL of ether was dropped a solution of 2.88 g (0.015 mol) of *exo*-2-acetoxy-4-homobrendane (**9**) in 10 mL of ether, and the reaction mixture was stirred for a further 2 h under reflux. After any unreacted lithium aluminum hydride was decomposed by the addition of water, the reaction mixture was mixed with 1 mL of 3 N sodium hydroxide solution, and then with 3 mL of water. The mixture was extracted with four 50-mL portions of ether. The combined ether extracts were washed with two 50-mL portions of water and dried over anhydrous sodium sulfate. Evaporation of ether gave 2.13 g (95% yield) of the colorless solid of crude *exo*-2-hydroxy-4-homobrendane (**10**). Purification on preparative VPC gave a pure sample: mp 128.5–129.5 °C (sealed tube) (lit.[12] 127–129 °C); IR (Nujol) 3300 br, 2950, 1062, 1058, 1008 cm^{-1} [lit.[12] ($CDCl_3$) 1065, 1055 cm^{-1}]; ^1H NMR ($CDCl_3$) δ 0.6–2.2 (m, 15), 3.43 (br s, 1); mass spectrum *m/e* (rel intensity) 152 (13, M^+), 134 (100), 121 (43), 95 (49), 92 (33), 81 (56), 80 (31), 79 (36), 67 (46), 57 (29).

4-Homobrendan-2-one (11). To a solution of 1.94 g (0.013 mol) of *exo*-2-hydroxy-4-homobrendane (**10**) in 20 mL of acetone kept at 0 °C was added dropwise a mixture of 1 g of chromium trioxide, 1 mL of 95% sulfuric acid, and 10 mL of water in a period of 15 min. The reaction mixture was stirred for a further 2 h at the same temperature. Excess chromium trioxide was decomposed by a sodium hydrogen sulfite solution. The mixture was extracted with three 50-mL portions of ether, and the combined ether extracts were washed with two 50-mL portions of water. The ether solution was dried over anhydrous sodium sulfate and concentrated to give 1.89 g (98% yield) of crude 4-homobrendan-2-one (**11**). Purification on preparative VPC gave a pure sample: mp 125–127 °C (sealed tube) (lit.[12] 122–124 °C); IR (Nujol) 1750, 1170, 1100, 1000, 830, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.6 (complex m); mass spectrum *m/e* (rel intensity) 150 (58, M^+), 132 (18), 119 (22), 104 (19), 94 (24), 93 (38), 83 (22), 81 (100), 80 (47), 79 (45).

4-Homobrendane (12). A mixture of 0.45 g (0.003 mol) of 4-homobrendan-2-one (**11**), 10 g of potassium hydroxide, 11 mL of 100% hydrazine hydrate, and 40 mL of diethylene glycol was treated similarly as for the preparation of 2,10-dehydro-4-homobrendane (**8**). Concentration of the *n*-hexane solution gave 0.32 g (78% yield) of crude 4-homobrendane (**12**), which was purified by sublimation to give a pure sample: mp 65–67 °C; IR (neat) 2930, 1450, 1300, 1100, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.2 (complex m); ^{13}C NMR ($CDCl_3$) δ_C 14.3 (t, 1, C-5), 27.1 (t, 2, C-2 and C-10, or C-4 and C-6), 33.7 (t, 2, C-2 and C-10, or C-4 and C-6), 33.9 (d, 2, C-3 and C-7), 37.8 (d, 1, C-1), 41.9 (d and t, 2, C-8 and C-9); mass spectrum *m/e* (rel intensity) 136[14] (100, M^+), 121 (46), 95 (77), 94 (77), 93 (37), 80 (32), 79 (42), 67 (43), 41 (38), 18 (82).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.4; H, 11.9.

2-Cyano-2-trimethylsilyloxy-4-homobrendane (13). A solution of 3.0 g (0.02 mol) of 4-homobrendan-2-one (**11**) and 3.0 g (0.03 mol) of trimethylsilyl cyanide[15] in 20 mL of benzene containing a trace of zinc iodide was stirred at room temperature for 4 h. Evaporation of

benzene under slightly diminished pressure gave a quantitative yield of crude 2-cyano-2-trimethylsilyloxy-4-homobrendane (**13**): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H, CH_3Si), 0.9–2.5 (complex m, 14 H); mass spectrum *m/e* (rel intensity) 249 (20, M^+), 234 (31), 221 (20), 159 (20), 155 (20), 121 (51), 95 (100), 79 (22), 75 (26), 73 (68), 55 (23), 41 (24).

2-Aminomethyl-2-hydroxy-4-homobrendane (14) and Its Hydrochloride (14 HCl). To a suspension of 3.79 g (0.1 mol) of lithium aluminum hydride in 30 mL of ether was added with stirring a solution of crude 2-cyano-2-trimethylsilyloxy-4-homobrendane (**13**) in 30 mL of ether. The reaction mixture was stirred for 3 h under reflux. The cooled reaction mixture was treated successively with 4 mL of water, 4 mL of 3 N sodium hydroxide solution, and 12 mL of water. The mixture was filtered, and the precipitates were washed with three 30-mL portions of ether. The combined filtrate and washings were dried over anhydrous sodium sulfate and concentrated. The residue was found to give only one major peak on conventional VPC. Purification of a portion of the residue on preparative VPC afforded a pure sample of 2-aminomethyl-2-hydroxy-4-homobrendane (**14**): IR (neat) 3600–3200, 1600, 1050, 940 cm^{-1}; mass spectrum *m/e* (rel intensity) 181 (29, M^+), 151 (100), 150 (65), 133 (39), 95 (28), 91 (51), 81 (54), 79 (32), 67 (35), 41 (36).

The crude **14** thus obtained (3.6 g, 0.02 mol) was dissolved in 50 mL of dry ether, and dry hydrogen chloride was bubbled through the solution for 2 h. Precipitates formed were filtered, washed with ether, and dried in vacuo to give 3.79 g [87% overall yield from 4-homobrendan-2-one (**11**)] of crude 2-aminomethyl-2-hydroxy-4-homobrendane hydrochloride (**14** HCl). Purification by recrystallization from methanol–acetone mixture afforded a pure sample: mp 278–281 °C dec (sealed tube); IR (Nujol) 3230, 3140, 2600, 1610, 1110, 1040 cm^{-1}.

Anal. Calcd for $C_{11}H_{20}NOCl$: C, 60.68; H, 9.26; N, 6.43; Cl, 16.28. Found: C, 60.4; H, 9.6; N, 6.4; Cl, 16.7.

2,4-Bishomobrendan-2-one (15). 2-Aminomethyl-2-hydroxy-4-homobrendane hydrochloride (**14** HCl, 3.35 g, 0.015 mol) and 1.3 g (0.016 mol) of anhydrous sodium acetate were dissolved in a mixture of 3 mL of acetic acid and 20 mL of water. To the solution was added dropwise a solution of 1.28 g (0.019 mol) of sodium nitrite in 10 mL of water, while the reaction temperature was kept below 20 °C. The reaction mixture was stirred at ambient temperature for an additional 2.5 h. The mixture was extracted with three 50-mL portions of ether. The combined ether extracts were washed with a saturated sodium hydrogen carbonate solution and then with two 20-mL portions of saturated sodium chloride solution. The ether solution was dried over anhydrous sodium sulfate and concentrated to give 1.4 g (58% yield) of crude 2,4-bishomobrendan-2-one (**15**). VPC purification of the crude **15** gave a pure sample: mp 81–82 °C; IR (Nujol) 1720, 1240, 1110, 1020, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–2.8 (complex m); ^{13}C NMR ($CDCl_3$) δ_C 14.0 (t), 26.2 (t), 30.5 (t), 30.9 (t), 31.3 (d), 36.4 (d), 36.7 (t), 38.9 (t), 39.1 (d), 49.7 (d), 214.8 (s); mass spectrum *m/e* (rel intensity) 164 (50, M^+), 120 (100), 106 (49), 93 (27), 81 (28), 80 (27), 79 (43), 67 (42), 41 (35), 39 (28).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.4; H, 9.6.

2,4-Bishomobrendane (4). A mixture comprising 1.46 g (0.09 mol) of 2,4-bishomobrendan-2-one (**15**), 3 g of potassium hydroxide, 2 g (0.04 mol) of 100% hydrazine hydrate, and 20 mL of diethylene glycol was treated similarly as for the preparation of 2,10-dehydro-4-homobrendane (**8**). The hexane solution was concentrated to give 0.87 g (65% yield) of crude 2,4-bishomobrendane (**4**). A pure sample of **4** was obtained by VPC fractionation: mp 69–71 °C (sealed tube); IR (Nujol) 2690, 1250, 1010, 990, 940, 910, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.9–2.3 (complex m); ^{13}C NMR ($CDCl_3$) δ_C 15.5 (t), 22.3 (t), 27.2 (t), 30.5 (t), 31.6 (t), 32.1 (d), 33.0 (t), 33.9 (d), 37.8 (d), 40.3 (t), 40.9 (d); mass spectrum *m/e* (rel intensity) 150 (100, M^+), 135 (37), 122 (46), 121 (81), 94 (34), 93 (37), 81 (45), 79 (50), 67 (48), 41 (40).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.7; H, 12.2.

Hydride Transfer Reduction–Rearrangement. A reactant (0.1 g) dissolved in 5 mL of *n*-pentane was mixed with 1 g of 95% sulfuric acid, and the mixture was stirred vigorously at room temperature. The reaction of 2,4-dehydro-4-homotwistane (**1**) was allowed to run for 30 min, and that of *exo*-2-hydroxy-4-homoisotwistane (**18**) for 5 min. The pentane layer was separated, washed with water, and dried over anhydrous sodium sulfate. The dried pentane solution was analyzed on Golay GC/MS for product distribution. Pentane was evaporated off from the solution to measure the yield of products.

Registry No.—**4,** 51027-87-3; **7,** 61559-33-9; **8;** 7203-36-3; **9,** 61559-34-0; **10,** 50529-94-7; **11,** 50529-80-1; **12,** 49700-65-4; **13,** 61559-35-1; **14,** 61559-36-2; **14** HCl, 61586-61-6; **15,** 61559-37-3.

References and Notes

(1) A. Krantz and C. Y. Lin, *J. Am. Chem. Soc.*, **95,** 5662 (1973); *Chem. Commun.*, 1287 (1971).
(2) (a) J. S. Wishnok, P. v. R. Schleyer, E. Funke, G. D. Pandit, R. O. Williams, and A. Nickon, *J. Org. Chem.*, **38,** 539 (1973); (b) A. Nickon and J. H. Hammons, *J. Am. Chem. Soc.*, **86,** 3322 (1964); (c) L. A. Paquette, G. R. Krow, J. M. Bollinger, and G. A. Olah, *ibid.*, **90,** 7147 (1968); V. Y. Merritt, J. Cornelisse, and R. Srinivasan, *ibid.*, **95,** 8250 (1973); J. E. McMurray, *J. Org. Chem.*, **36,** 2826 (1971); A. C. Udding, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 1345 (1968); H. Bos and G. W. Klumpp, *ibid.*, 3641 (1974); K. B. Wiberg, *Adv. Alicyclic Chem.*, **2,** 185 (1968).
(3) (a) N. Takaishi, Y. Inamoto, K. Tsuchihashi, K. Yashima, and K. Aigami, *J. Org. Chem.*, **40,** 2929 (1975); (b) N. Takaishi, Y. Inamoto, and K. Aigami, *ibid.*, 276 (1975); (c) N. Takaishi, Y. Inamoto, K. Aigami, and E. Ōsawa, *ibid.*, 1483 (1975).
(4) The corresponding hydrocarbon has been prepared by Cupas.[5]
(5) C. A. Cupas, W. E. Heyd, and M.-S. Kong, *J. Am. Chem. Soc.*, **93,** 4623 (1971).
(6) R. Yamaguchi and M. Kawanisi, *Chem. Lett.*, 649 (1975).
(7) K. M. Majerski and Z. Majerski, *Tetrahedron Lett.*, 4915 (1973); K. Mlinaric-Majerski, Z. Majerski, and E. Pretsch, *J. Org. Chem.*, **40,** 3772 (1975); **41,** 686 (1976).
(8) N. Takaishi, Y. Inamoto, K. Tsuchihashi, K. Aigami, and Y. Fujikura, *J. Org. Chem.*, **41,** 771 (1976), and references cited therein.
(9) Y. Inamoto, N. Takaishi, Y. Fujikura, K. Aigami, and K. Tsuchihashi, *Chem. Lett.*, 631 (1976).
(10) P. v. R. Schleyer, K. R. Blanchard, and C. D. Woody, *J. Am. Chem. Soc.*, **85,** 1358 (1963); G. A. Olah, J. M. Bollinger, and D. P. Kelly, *ibid.*, **92,** 1432 (1970).
(11) H. K. Hall, Jr., *J. Org. Chem.*, **25,** 42 (1960).
(12) G. N. Schrauzer, *J. Am. Chem. Soc.*, **81,** 5310 (1959).
(13) J. G. Henkel and A. Spurlock, *J. Am. Chem. Soc.*, **95,** 8339 (1973).
(14) E. M. Engler, M. Farcasiu, A. Sevin, J. M. Cense, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95,** 5769 (1973).
(15) J. N. Zubrick, B. I. Dunber, and H. D. Durst, *Tetrahedron Lett.*, 71 (1975).
(16) D. A. Evans, G. L. Carrol, and L. K. Truesdale, *J. Org. Chem.*, **39,** 914 (1974).
(17) M. A. McKinney and P. P. Patel, *J. Org. Chem.*, **38,** 4059 (1973).
(18) J. R. Wiseman and H. O. Krabbenhoft, *J. Org. Chem.*, **40,** 3222 (1975).
(19) N. Takaishi, Y. Fujikura, Y. Inamoto, H. Ikeda, and K. Aigami, *J. Chem. Soc., Chem. Commun.*, 372 (1975); K. Aigami, Y. Inamoto, N. Takaishi, Y. Fujikura, A. Takatsuki, and G. Tamura, *J. Med. Chem.*, **19,** 536 (1976).
(20) N. Takaishi, Y. Inamoto, Y. Fujikura, K. Aigami, B. Golicnik, K. Mlinaric-Majerski, Z. Majerski, E. Osawa, and P. v. R. Schleyer, *Chem. Lett.*, 763 (1976).
(21) E. Osawa, K. Aigami, N. Takaishi, Y. Inamoto, Y. Fujikura, Z. Majerski, P. v. R. Schleyer, E. M. Engler, and M. Farcasiu, to be published.