Registry No.—**42,** 3332-08-9; hexamethyldisilazane, 999-97-3; diisopropylamine, 108-18-9; 1-trimethylsiloxy-4-methoxycyclopentadiene, 66057-27-0; *endo,cis*-2-methoxy-3-hydroxybicyclo[2.2.1]heptane, 53329-03-6; *exo,cis*-2-methoxy-3-hydroxybicyclo[2.2.1]heptane, 53329-04-7; *cis*-1,2-cyclopentanediol, 5057-98-7; *cis*-2-methoxycyclopentanol, 13051-91-7; tetramethylpiperidine, 768-66-1; 2,2-dimethoxycyclopentanol, 63703-33-3; 2,2-dimethoxycyclohexanol, 63703-34-4.

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(24) **Note Added in Proof.** We have found that even cyclohexanone, when treated with LDA as described for **4,** affords 34% reduction. The ratio of reduction to enolization appears sensitive to both solvent (more reduction in ether than in THF) and to the nature of the commercial alkyllithium reagent used to prepare the LDA (more reduction with methyllithium containing lithium bromide than when prepared from *n*-butyllithium).

Hydride Transfer Reduction–Rearrangement of 4-Homobrendylcarbinols. Concomitant Ring Enlargement and Skeletal Isomerization in a Tricyclic 2-Norbornylcarbinyl System

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Received August 31, 1977

By the brief contact with 95% sulfuric acid and *n*-pentane, 4-homobrend-3-ylcarbinol (**4**) was transformed predominantly into 4-homoisotwistane (**15**), while 2-methyl-4-homobrendan-2-ol (**11**) gave exclusively a mixture of 1- and 2-methyladamantane. 4-Homobrend-*exo*- and -*endo*-2-ylcarbinol (**9x** and **9n**) afforded both **15** and methyladamantanes. **9x** gave also the simple reduction product *exo*-2-methyl-4-homobrendane (**10x**), whereas **9n** did not give the corresponding product (**10n**). The ratio of **15** to combined 1- and 2-methyladamantane, which represented the relative importance of the ring enlargement process vs. the rearrangement of the 4-homobrendane skeleton in **9x** and **9n,** was much larger for **9x** than for **9n.** The result was successfully interpreted with consideration of the relative stabilities of the intermediate bridged cations involved in the ring enlargement.

We had been looking for synthetic routes to 2,4-bishomobrendane (tricyclo[6.2.1.$0^{4,9}$]undecane, **16**), an unknown compound presumed to intervene in some key steps of the acid-catalyzed skeletal rearrangement of tricycloundecane.[1] Hydride transfer reduction–rearrangement[2] of 4-homobrend-2- and -3-ylcarbinols (tricyclo[5.2.1.$0^{3,8}$]dec-2- and -3-ylcarbinols, **9x, 9n,** and **4,** Scheme I) was thought promising in view of the well-documented ring enlargement of the 2-norbornylcarbinyl to the bicyclo[3.2.1]octyl cation.[3,4] In actuality, however, the method failed to give the hoped-for 2,4-bishomobrendane,[5] but produced 4-homoisotwistane (tricyclo[5.3.1.$0^{3,8}$]undecane, **15**), a twice-rearranged ring enlargement product, together with 1- and 2-methyladamantane. Concomitant formation of methyladamantanes indicated, as discussed below, the ring enlargement to be partly inhibited in 4-homobrendylcarbinols. The only example of the inhibition of ring enlargement in the 2-norbornylcarbinyl system has been reported hitherto by Whittaker[6] for the acetolysis of 3,3-dimethylnorborn-*endo*-2-ylcarbinyl tosylate. The extent of the inhibition of the ring enlargement in the present 4-homobrendylcarbinyl system was found at variance with the structures and configurations of the carbinols, and these results were successfully interpreted in terms of the stability of the bridged cationic intermediate involved in the ring enlargement process.

Results

Synthesis. Three tricyclic carbinols, 4-homobrend-3-, -*exo*-2-, and -*endo*-2-ylcarbinol (**4, 9x,** and **9n,** respectively), as well as 2-methyl-4-homobrendan-2-ol (**11**) of undetermined configuration, were prepared according to the routes shown in Scheme I. Bromination[7] of 4-homobrendane (**1**)[2a,8] gave exclusively the 3-bromide **2.**[8,9] Its structure was determined unequivocally by ^{13}C NMR spectrometry and lithium–*tert*-butyl alcohol reduction. Ten signals including the lowest field singlet in the ^{13}C NMR spectrum indicated the bromide to be an asymmetrical bridgehead-substituted derivative. Reduction by lithium in *tert*-butyl alcohol reverted the bromide back to the original hydrocarbon **1** to demonstrate the intactness of the skeleton during the bromination. Koch carboxylation of **2** gave the corresponding acid **3,** and the structure of **3** was established by the formation of the same 3-ol **5**[10]

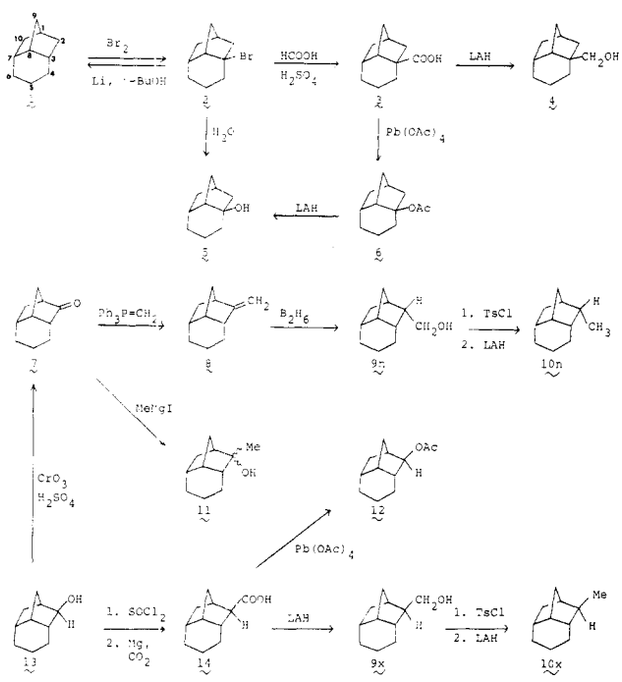
0022-3263/78/1943-2608$01.00/0

Table I. Product Distribution in the Hydride Transfer Reduction–Rearrangement of 4-Homobrendylcarbinols and Methyl-4-homobrendanol[a]

Run	Reactant	Reaction time, min	Yield, %	Product, %[b] 15[c]	2-Me-Ad	1-Me-Ad	Others
1	**4**	5	62	93.1	0.8		2.0,[d] 0.4[e]
2		30	63	85.6	3.1	0.4	0.6,[d] 1.8[e]
11	**9x**	5	47	42.5	24.8	2.3	19.7[f]
12		10	*g*	38.8	28.3	2.7	19.5[f]
13		30	*g*	36.0	32.6	3.2	17.9[f]
14		60	50	30.9	40.4	3.8	13.9[f]
21	**9n**	5	36	6.7	79.3	5.9	
22		30	39	6.6	81.8	8.1	
31	**9n + 10n**	5	52	3.4	50.4	3.1	36.1[h]
32	(1:0.3)[i]	10	*g*	2.9	57.0	4.3	26.9[h]
33		30	*g*	2.8	73.4	5.9	8.3[h]
34		60	52	2.4	83.6	6.7	0.2[h]
41	**11**	5	43		79.9	8.3	
42		30	47		74.3	13.6	

[a] 100 mg of reactant, 1 g of 95% sulfuric acid, and 5 mL of *n*-pentane stirred vigorously at room temperature (~25 °C). [b] Calculated from VPC peak areas. Balance consists of several unidentified compounds. [c] Containing a little *endo*-2,8-trimethylenebicyclo[3.3.0]-octane[1b] as shown by the blip of VPC peak. [d] 2,4-Bishomobrendane (**16**).[2a] [e] Homoadamantane. [f] *exo*-2-Methyl-4-homobrendane (**10x**). [g] Not determined. [h] *endo*-2-Methyl-4-homobrendane (**10n**). [i] A mixture of 4-homobrend-*endo*-2-ylcarbinol (**9n**) and *endo*-2-methyl-4-homobrendane (**10n**) in 1:0.3 molar ratio.

Scheme I



either from the acid via the acetate **6**[10] or directly from the bromide **2.** Reduction of the acid **3** gave the desired 3-ylcarbinol **4.**

Hydroboration of 2-methylene-4-homobrendane (**8**), prepared from the corresponding ketone (**7**)[2a,11] by a Wittig reaction, gave almost exclusively a primary alcohol, as indicated by ^1H and ^{13}C NMR. On the basis of predominant exo attack of diborane, as has been mostly the case for polycyclic olefins for steric reasons,[12] an endo configuration **9n** was assigned to the alcohol. The corresponding hydrocarbon, *endo*-2-methyl-4-homobrendane (**10n**), was prepared from **9n** by tosylation and subsequent lithium aluminum hydride reduction.

A 4-homobrendane-2-carboxylic acid (**14**) was obtained from the *exo*-2-ol **13**[2a,11] via treatment with thionyl chloride and Grignard carboxylation. The structure of **14** was proved by lead tetraacetate decarboxylation, leading to the *exo*-2-yl acetate (**12**) of established structure.[2a,11] Lithium aluminum hydride reduction of **14** gave a 2-ylcarbinol (**9x**), which was different from the endo isomer **9n** prepared above. Accordingly, an exo configuration was assigned to **9x.** The acid **14** then should also be the exo isomer. *exo*-2-Methyl-4-homobrendane (**10x**) was prepared from **9x** by the same procedure as that for **10n.**

The above configurational assignments for **9x, 9n, 10x, 10n,** and **14** are consistent with their ^{13}C NMR spectra. All the exo isomers, **9x, 10x,** and **14,** exhibit abnormally high-field (~15 ppm) methylene carbon signals which have been attributed to arise from steric compressions exerted by endo hydrogens (*endo*-2- and -10-H) on the two *β-axial*-methylene substituents.[1,2a] In contrast to this, the highest field triplet (methylene) signals in the spectra of endo isomer **9n** and **10n** are 18.52 and 18.32 ppm, respectively.

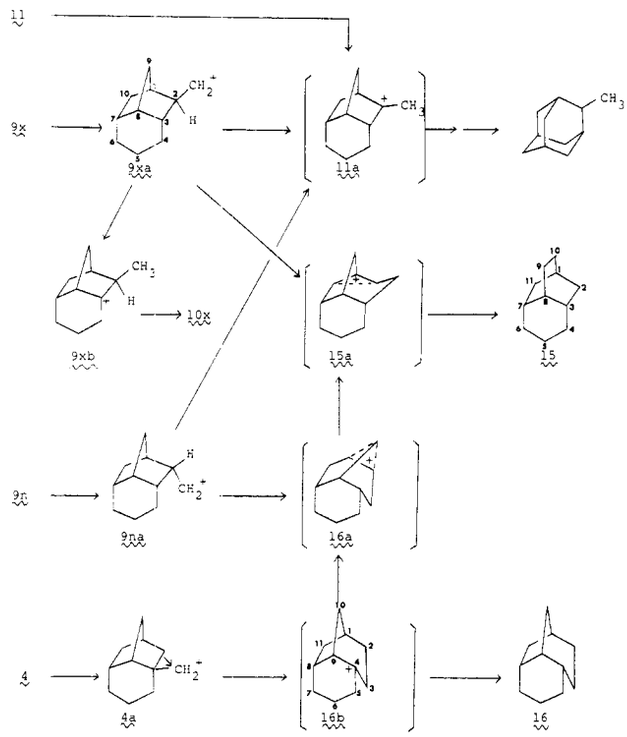
Reaction of methylmagnesium iodide with 4-homobrendan-2-one (**7**) gave a 2-methyl-2-hydroxy-4-homobrendane (**11**). The configuration of the substituents in **11** would most probably be *exo*-methyl-*endo*-hydroxy, for the reasons of predominant exo attack of the Grignard reagent.[13]

Hydride Transfer Reduction–Rearrangement. The alcohols thus obtained were stirred with 95% sulfuric acid and *n*-pentane at room temperature. Analysis and identification of the products were made on Golay GC–MS.[1,2] The reactions were almost complete in 5 min, giving pentane-soluble products in 36–62% yields, and longer reactions caused only secondary conversions of the products accompanied by a few percent increases in yields. For every reaction, several unidentified compounds (*m/e* 150 or 148) were detected which amounted to ~10% of the total products. The number of these unidentified products varied from eight to ten depending upon the precursor alcohols used. The results are summarized in Table I.

The bridgehead carbinol **4** underwent almost exclusively ring enlargement, leading to 4-homoisotwistane (**15**). 2,4-Bishomobrendane (**16**) was detected only in the reaction of this carbinol **4.** In contrast to **4,** the tertiary alcohol **11** gave only methyladamantanes, showing no sign of the ring enlargement.

The 2-ylcarbinol **9x** and **9n** reacted along both directions to afford **15** and methyladamantanes. However, the exo isomer

Scheme II



9x showed a larger tendency to ring enlargement than to the methyladamantane formation (run 11), while the endo isomer **9n** behaved oppositely (run 21). It is also to be noted that the simple hydride-transfer reduction product (**10x**) was formed as a major product only in the reaction of the exo isomer **9x.**

Isomerization of this reduction product **10x** was fairly slow compared to that of the carbinol itself, only 30% of **10x** having disappeared after 60 min of reaction (run 14). The once formed hydrocarbon **10x,** therefore, can not be an intermediate to methyladamantanes in the fast rearrangement of **9x.** The *endo*-methyl isomer **10n,** although it was not detected in the reaction of **9n,** could intervene in the route from **9n** to methyladamantanes, if it reacts very fast. To test this possibility, isomerization of **10n** was also examined. Since 95% sulfuric acid alone did not cause the rearrangement of **10n** appreciably, the corresponding carbinol **9n** was also added as a carbocation source (runs 31–34). Rearrangement of **10n** was much faster than that of the exo isomer **10x,** yet too slow to be considered as an intervening process to methyladamantanes.

Discussion

Ring enlargement leading to 4-homoisotwistane (**15**) was an almost exclusive reaction pathway in the bridgehead carbinol **4.** Detection of a small amount of 2,4-bishomobrendane (**16**), combined with the established high reactivity of **16** and its transformation into **15,**[1b] indicated that the shift of C-2 to give 2,4-bishomobrend-4-yl cation (**16b,** Scheme II) was the predominant process in the reaction of **4a.** Other possible ring enlargements in **4a,** shifts of C-4 and C-8, produce *endo*-2,6-tetramethylenenorbornane (tricyclo[6.2.1.$0^{3,9}$]undecane) and 4-homoprotoadamantane (tricyclo[5.3.1.$0^{3,9}$]undecane), respectively, which are more strained than **16.**[14] These processes, therefore, should be less likely to occur.

1,3-Transfer of 2-H's and 4-H's in **4a** are stereoelectonically[14] allowable to give 3-methyl-4-homobrend-2- and -4-yl cation, respectively, and the latter cation should afford[8,14] methyladamantanes through the shift of C-2 to 7-methylprotoadamantane. However, these hydride transfers were not actually realized. Similar preference to 1,2-alkyl shift over 1,3-hydride transfer was observed for the competitive rearrangement of 2,4-bishomobrend-10-yl (**16**-10-yl) cation which gave predominantly *endo*-2,8-ethano-*cis*-bicyclo[3.3.0]octane (tricyclo[5.3.1.$0^{4,11}$]undecane) over 4-homoisotwistane (**15**) formed via the **16**-2-yl cation.[1b] The shift of C-2 in **4a** would be further favored by the formation of a bridgehead cation **16b,** as compared to hydride transfers which give secondary (bridge) 2- and 4-yl cations.

The tertiary alcohol **11** gave only methyladamantanes. This rearrangement pathway would be explained most reasonably with the intermediacy of a methylprotoadamantane[14] (*exo*-10-methylprotoadamantane) formed from the cation **11a** by the 1,3-transfer of *endo*-4-H to give the **10x**-4-yl cation followed by the shift of methyl-bearing C-2 in the latter cation. Thus the ring enlargement by the incorporation of the methyl group did not occur at all in **11.** This is another example of "no return of methyl group"[14,15] once extruded out the tricycloundecane ring systems.

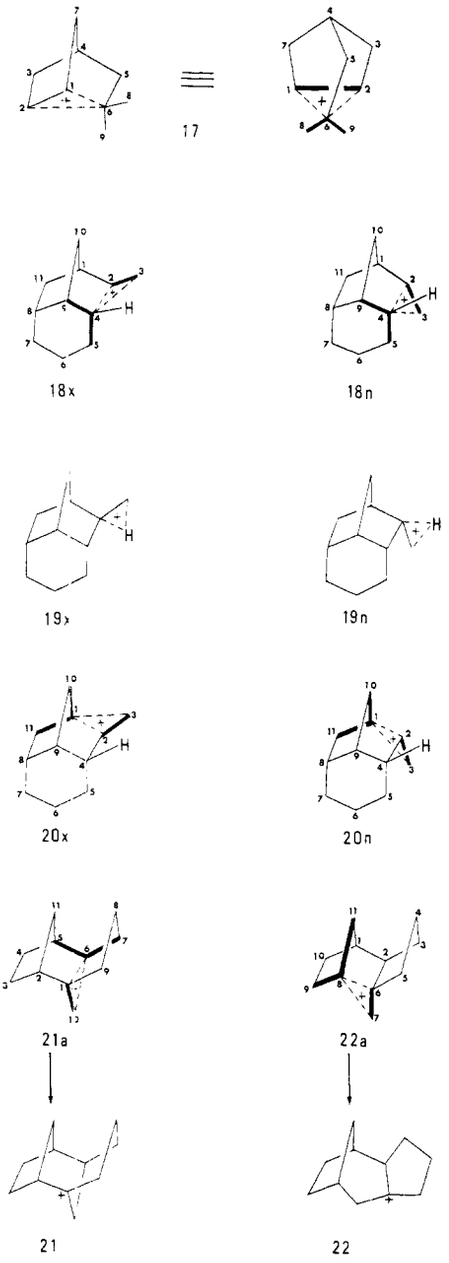
The 2-ylcarbinols, **9x** and **9n,** gave not only 4-homoisotwistane (**15**), but methyladamantanes. These methyladamantanes must be produced mainly by direct isomerization of the 4-homobrendane skeleton in **9x** and **9n,** because the ring enlargement product **15** did not rearrange easily under the present reaction conditions (cf. run 2, Table I). The pathway to methyladamantanes in **9x** and **9n** is presumed to be the same as that in **11,** since a similar ratio (~10:1) of 2- to 1-methyladamatane was found for these precursors (runs 11, 21, and 41). The cation **9xa** and **9na** are connected to **11a** by 1,2-hydride transfers (Scheme II), and these processes should be favorable because of the formation of a stable, tertiary cation.

Ratio of the ring enlargement to the skeletal rearrangement, as measured by the ratio of **15** to combined methyladamantanes, was largely different in the two 2-ylcarbinols, the stronger tendency to ring enlargement than to skeletal rearrangement being noticed in the exo isomer **9x.** The change in the ratios of the two processes with the configuration of the 2-ylcarbinols appears to be interpreted with the relative stabilities of the transition states (or intermediate cationic species), as discussed below.

Schleyer[16] found ~20 times deceleration of solvolysis rates in 6,6-dimethyl-2-norbornyl tosylates as compared to those in the unsubstituted compounds, and attributed the cause to destabilization of the transition state (or bridged intermediate cation) by steric repulsion exerted by the two methyl groups (**17,** Scheme III). Whittaker[6] gave an interpretation in terms of this steric destabilization for the inhibition of the ring enlargement in 3,3-dimethylnorborn-*endo*-2-ylcarbinyl cation. On the other hand, Sauers[17] ascribed the preferable migration of methylene over that of methine in Baeyer–Villiger oxidation of substituted 2-norbornanones to the relief of torsional strain, which was realized only in the methylene migration transition state. McKinney[3d] referred to this explanation in the interpretation of the well-known preference for methylene migration in 2-norbornylcarbinyl ring enlargements. "Tortional strain relief" and "steric destabilization" are two different expressions for the same concept, and we consider that this concept is also applicable to the interpretation of the present variation in the extent of ring enlargement in **9x** and **9n.**

The transition state for the ring enlargement in the exo carbinol **9x** would be represented by **18x** (Scheme III), and that in **9n** by **18n.** In **18n,** the two substituents, C-5 and C-9, on the bridging carbon atom C-4 are situated close to the plane of the bridge and, hence, to C-3 and C-2, respectively. The geometry of these atoms here is quite similar to that in **17,** and we may call this geometry a *parallel* disposition (of C-1–C-2 and C-8–C-9 in **17** and C-2–C-3 and C-5–C-9 in **18n**). In contrast to **18n, 18x** has a *perpendicular* arrangement of C-5–C-9

Scheme III



with respect to C-2–C-3, resulting in C-5 and C-9 apart and away from C-2 and C-3. Then steric repulsions around the cationic center would be larger in **18n** than in **18x,** and the energy difference between **18n** and **18x** may be expected to exceed that between the ground state **9n** and **9x.** On the other hand, the transition state for the first step of the skeletal rearrangement, 1,2-transfer of the 2-hydride to give **11a,** would be **19x** for **9x** and **19n** for **9n.** The activation energy should be similar for these processes, as the transition state retains essentially the same configuration as that in the ground state for each carbinol. Therefore, the ring enlargement in **9x** via **18x** would be more likely to occur than that in **9n** via **18n.**

It might seem that the possibility remains for the ring enlargement in **9x** and **9n** by the shift of C-1 in place of C-3. However, transition states for the shift of C-1, **20x** and **20n,** have parallel geometries something like **18n,** which render these processes less likely to occur.

The same concept appears to explain why ring enlargement in *exo*-2,3-trimethylenenorborn-*endo*-2-ylcarbinol gave exclusively *exo*-2,4-ethanobicyclo[3.3.1]nonane (tricyclo[4.3.1.$1^{2,5}$]undecane, **21**),[15] although it is less stable[14] than *exo*-2,3-trimethylenebicyclo[3.2.1]octane (tricyclo[6.2.1.$0^{2,6}$]undecane, **22**).[2b] A perpendicular transition state (**21a**) is involved in the route to the former compound, whereas a parallel one (**22a**) is involved in that to the latter.

Another major difference between the reactions of **9x** and **9n** is formation of the simple reduction product, 2-methyl-4-homobrendane (**10x**), only from the exo compound **9x.** The explanation seems to lie in that only **9x** can give rise by 1,3-hydride transfer to the stable 3-yl cation[10] **9xb** which undergoes skeletal rearrangement with difficulty. Suppression of 1,3-transfer of 3-H in **9n** appears to result from an unfavorable orbital overlap between 3-H and the vacant p orbital on the cationic carbon atom. Stability of the bridgehead cation **9xb,** on the other hand, would be understood from the reasoning stated below.

Any of the shifts of β-carbon atoms of **9xb,** C-1, C-5, C-7, and C-9, to the cationic C-3 center produces skeletal structures more strained than 4-homobrendane.[8-14] In addition, all the hydride transfers stereoelectronically conceivable[14] in **9xb,** 1,2-transfer of *endo*-2-H, 4-H's, and 8-H as well as 1,3-transfer of *syn*-9-H, are definitely unfavorable. 1,2-Transfers to the bridgehead C-3 cationic center should trespass through a highly strained transition state involving ethyleneprotonium bridging to the bridgehead.[18] 1,3-Transfer of *syn*-9-H may be kinetically allowable. However, this process produces less stable, secondary **10x**-9-yl cation and, moreover, all the alkyl shifts in **10x**-9-yl cation lead to more strained, cyclobutane-containing structures. Therefore, the 1,3-transfer of *syn*-9-H should be less likely to occur.[1b] The cation **9xb** is thus considered to have little capability for further skeletal rearrangement. In other words, the cation is situated in a "local minimum" on the rearrangement energy surface.[8,14,15]

Experimental Section

All melting and boiling points are uncorrected. Measurements of IR, ^{1}H and ^{13}C NMR, and mass spectra as well as conventional and preparative VPC and Golay column GC–MS measurements were done on the same instruments as in the previous works.[1,2]

4-Homobrendane (**1**), 4-homobrendan-2-one (**7**), and *exo*-2-hydroxy-4-homobrendane (**13**) were prepared according to our previous methods.[2a]

3-Bromo-4-homobrendane (2). 4-Homobrendane (5 g, 0.037 mol) was stirred with 50 g (0.31 mol) of bromine at room temperature for 25 min. Excess bromine was evaporated off in vacuo, and the residue was taken up in carbon tetrachloride. The solution was washed with a saturated sodium bisulfite solution and water and dried over anhydrous magnesium sulfate. Evaporation of the carbon tetrachloride and sublimation of the residue gave 4.2 g (52% yield) of pure 3-bromo-4-homobrendane (**2**): mp 59–60 °C (sealed tube); ^{13}C NMR ($CDCl_3$) δ_C 19.17 (t), 26.15 (t), 31.88 (t), 35.86 (d), 38.46 (d), 40.69 (t and t), 47.82 (t), 53.20 (d), 75.04 (s); mass spectrum *m/e* (rel intensity) 215 (4, M^+), 213 (4, M^+), 136 (18), 135 (100), 134 (23), 119 (16), 93 (42), 92 (26), 91 (49), 80 (74), 79 (64), 77 (36), 67 (56).

Anal. Calcd for $C_{10}H_{15}Br$: C, 55.81; H, 6.97; Br, 37.22. Found: C, 56.01; H, 7.11; Br, 36.9.

Hydrolysis of **2** in acetone–water at reflux[7] overnight in the presence of 2 equiv of sodium carbonate followed by purification by sublimation gave 3-hydroxy-4-homobrendane (**5**) in 88% yield: mp 161–162 °C (sealed tube) (lit.[10] mp 161–162 °C); IR (neat) 3350, 1120, 1110, 1090, 980, 890 cm^{-1}; mass spectrum *m/e* (rel intensity) 152 (100, M^+), 137 (15), 134 (16), 124 (20), 119 (16), 111 (17), 110 (36), 109 (45), 108 (18), 97 (90).

4-Homobrendane-3-carboxylic Acid (3). A solution of 3.0 g (0.014 mol) of the bromide **2** in 30 mL (0.79 mol) of 99% formic acid was added dropwise with efficient stirring over a period of 30 min to 50 mL of 95% sulfuric acid kept at 0–5 °C. The reaction was stirred for an additional 2 h at the same temperature, and the reaction mixture was poured onto 500 mL of ice–water. Crude 4-homobrendane-3-carboxylic acid (**3,** 1.8 g, 71% yield) was isolated by the same procedure as that for 4-homoisotwistane-3-carboxylic acid.[7] Purification by sublimation in vacuo gave a pure sample: mp 66–67 °C (sealed tube); IR (neat) 2650, 1690, 1450, 1400, 1290, 950 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1–2.2 (m, 15 H), 12.1 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ_C 15.26 (t), 26.35 (t), 30.78 (t), 32.97 (t), 33.25 (d), 36.75 (t), 37.23 (d), 40.60 (t), 44.10 (d), 49.29 (s), 186.08 (s); mass spectrum *m/e* (rel intensity) 180 (9, M^+), 136 (12), 135 (100), 93 (11), 79 (12), 67 (14).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.15; H, 9.03.

The acid thus obtained was decarboxylated to 4-homobrend-3-yl acetate (**6**) as follows. A mixture of 1.8 g (0.01 mol) of the acid **3**, 7.2 g (0.016 mol) of lead tetraacetate, 8.4 g (0.086 mol) of anhydrous potassium acetate, and 60 mL of glacial acetic acid was heated for 4 h under reflux with stirring. The mixture was concentrated in vacuo and the residue was extracted with three 20-mL portions of ether. The combined ether extracts were washed with a saturated sodium bicarbonate solution and water and dried over anhydrous sodium sulfate. Evaporation of the ether and purification of the residue by preparative VPC gave 0.87 g (45% yield) of 4-homobrend-3-yl acetate (**6**): IR (neat) 2950, 1730, 1370, 1260, 1250, 1220, 1070 cm^{-1} (lit.[10] 5.73 μm = 1745 cm^{-1}); ^1H NMR ($CDCl_3$) δ 0.9–2.5 (m), including 1.78 (s) (lit.[10] δ 1.0–2.4 (m) with s at 1.79); mass spectrum *m/e* (rel intensity) 194 (1, M^+), 152 (24), 135 (21), 134 (100), 119 (23), 106 (12), 105 (17), 97 (17), 92 (27), 80 (45).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.02; H, 9.48.

Reduction of 0.49 g (0.0025 mol) of the acetate **6** with 0.095 g (0.0025 mol) of lithium aluminum hydride in 10 mL of ether gave 0.35 g (92% yield) of 4-homobrendan-3-ol (**5**), which was identical with the sample obtained from the bromide **2** on comparison of spectra and mixture melting point determination.

4-Homobrend-3-ylcarbinol (4). A solution of 1.8 g (0.01 mol) of the carboxylic acid **3** in 10 mL of dry ether was added dropwise with stirring into a suspension of 0.57 g (0.015 mol) of lithium aluminum hydride in 20 mL of ether. The mixture was heated under reflux for 3 h, cooled, and treated with 1.8 mL of water, 1.8 mL of 3 N sodium hydroxide solution, and then 5.4 mL of water. The ether layer was separated and dried over anhydrous sodium sulfate. Evaporation of the ether and purification of the residue by sublimation in vacuo afforded 1.41 g (85% yield) of pure 4-homobrend-3-ylcarbinol (**4**): mp 90–91 °C (sealed tube); IR (neat) 3600, 1120, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.2 (m, 15 H), 2.80 (s, 1 H), 3.26 (q, 2 H); ^{13}C NMR ($CDCl_3$) δ_C 16.32 (t), 27.00 (t), 30.00 (t), 33.33 (t), 34.23 (d), 36.83 (t), 37.64 (d), 38.98 (t), 42.07 (s), 42.76 (d), 71.10 (t); mass spectrum *m/e* (rel intensity) 166 (1, M^+), 136 (29), 135 (100), 93 (35), 91 (16), 81 (23), 79 (36), 77 (16), 67 (57).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.52; H, 10.83.

2-Methylene-4-homobrendane (8). A solution of 21.4 g (0.060 mol) of methyltriphenylphosphonium bromide and 5.76 g (0.060 mol) of potassium *tert*-butoxide in 100 mL of Me_2SO was stirred at room temperature for 1 h. 4-Homobrendan-2-one (**7**, 6.0 g, 0.040 mol) was added dropwise with stirring to the above solution over a period of 1 h, and then the solution was heated to 150–160 °C for 3 h. The cooled reaction mixture was mixed with 100 mL of cold water and extracted with three 100-mL portions of *n*-pentane. The combined pentane extracts were washed with water and concentrated. The residue was passed through an alumina-packed column ($^3/_4$ in. × 1 ft) and eluted with *n*-pentane. Evaporation of the pentane gave 4.26 g (72% yield) of pure 2-methylene-4-homobrendane (**8**): IR (neat) 3070, 2940, 2860, 1670, 1450, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9–2.8 (m, 14 H), 4.60 (d, 1 H), 4.90 (d, 1 H); mass spectrum *m/e* (rel intensity) 148 (78, M^+), 119 (33), 107 (40), 105 (32), 94 (54), 92 (34), 91 (57), 80 (100), 79 (76), 77 (33).

Anal. Calcd for $C_{11}H_{16}$: C, 89.19; H, 10.81. Found: c, 88.98; H, 10.83.

4-Homobrend-*endo*-2-ylcarbinol (9n). Hydroboration of 3.52 g (0.024 mol) of the methylene-4-homobrendane **8** was carried out in the usual manner in 40 mL of THF with 1.8 g (0.048 mol) of sodium borohydride and 9.1 g (0.064 mol) of boron trifluoride etherate at ambient temperature for 30 min. Oxidation of the reaction mixture with 10 mL of 30% hydrogen peroxide and 10 mL of 3 N sodium hydroxide solution gave crude 4-homobrend-*endo*-2-ylcarbinol (**9n**). Purification by alumina column chromatography with *n*-pentane and ether as eluents afforded 2.8 g (71% yield) of a pure sample: mp 77–78 °C (sealed tube); IR (neat) 3250, 1030, 1000 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.0–2.2 (m, 16 H), 3.42 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ_C 18.52 (t), 24.24 (t), 25.83 (t), 26.68 (t), 33.22 (d), 34.44 (d), 39.35 (d), 40.93 (t), 43.13 (d), 46.98 (d), 60.55 (t); mass spectrum *m/e* (rel intensity) 166 (2, M^+), 148 (100), 135 (63), 133 (27), 120 (32), 119 (63), 107 (32), 106 (32), 105 (28), 95 (43), 94 (44), 93 (54), 92 (44), 91 (47), 81 (60), 80 (76), 79 (92).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.51; H, 11.00.

***endo*-2-Methyl-4-homobrendane (10n).** 4-Homobrend-*endo*-2-ylcarbinol (**9n**, 0.4 g, 0.0024 mol) was allowed to react with 0.50 g (0.0026 mol) of *p*-toluenesulfonyl chloride in 10 mL of pyridine at room temperature for 5 h to give 0.76 g (99% yield) of the crude tosylate of **9n**: IR (neat) 1360, 1190, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.2 (m, 15 H), 2.40 (s, 3 H), 4.21 (d, J = 7 Hz, 2 H), 7.1–7.6 (q, 4 H).

A sample (0.75 g, 0.0023 mol) of the tosylate obtained above was reduced with 0.18 g (0.0047 mol) of lithium aluminum hydride in 25 mL of ether. The crude product was purified by column chromatography (alumina–*n*-pentane) to give 0.30 g (85% yield) of pure *endo*-2-methyl-4-homobrendane (**10n**): mp 90–91 °C (sealed tube); ^1H NMR ($CDCl_3$) δ 0.9–1.8 (m); ^{13}C NMR ($CDCl_3$) δ_C 11.01 (q), 18.32 (t), 24.46 (t), 25.40 (t), 26.80 (t), 33.68 (d), 34.63 (d), 38.04 (d), 40.99 (t), 43.14 (d), 43.40 (d); mass spectrum *m/e* (rel intensity) 150 (100, M^+), 135 (55), 121 (81), 109 (40), 95 (68), 94 (55), 79 (57), 67 (48).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 88.01; H, 11.98.

2-Methyl-4-homobrendan-2-ol (11). A solution of methylmagnesium iodide was prepared from 8.0 g (0.066 mol) of methyl iodide and 1.6 g (0.066 mol) of magnesium foil in 10 mL of ether. To the solution was added dropwise with stirring a solution of 1.5 g (0.010 mol) of 4-homobrendan-2-one (**7**) in 5 mL of ether, and the reaction was heated under reflux for 2 h. The crude 2-methyl-4-homobrendan-2-ol (**11**) was purified by passage through an alumina column with ether as eluent to give 1.4 g (84% yield) of pure **11**: mp 45–46 °C (sealed tube); IR (neat) 3450, 2930, 1470, 1450, 1290, 1260, 1210, 1160, 1140, 1070, 1050, 1000, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.3 (m, with sharp s at 1.12); ^{13}C NMR ($CDCl_3$) δ_C 17.10 (t), 23.55 (t), 25.10 (q), 26.80 (t), 31.75 (d), 33.17 (t), 37.60 (t), 42.39 (d), 42.59 (d), 49.42 (d), 75.00 (s); mass spectrum *m/e* (rel intensity) 166 (22, M^+), 151 (14), 148 (63), 123 (36), 121 (13), 119 (22), 108 (56), 96 (21), 95 (32), 81 (81).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.52; H, 10.85.

4-Homobrendane-*exo*-2-carboxylic Acid (14). A mixture of 6.0 g (0.039 mol) of *exo*-2-hydroxy-4-homobrendane (**13**) and 50 mL of thionyl chloride was heated under reflux for 3 h. Excess thionyl chloride was evaporated off, finally azeotropically with benzene, and the residue was distilled in vacuo to give 3.0 g (45% yield) of 2-chloro-4-homobrendane: bp 57 °C (0.5 mm); ^1H NMR ($CDCl_3$) δ 1.0–2.2 (m, 14 H), 3.6 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ_C 14.86 (t), 24.89 (t), 26.67 (t), 30.94 (t), 32.12 (d), 38.25 (t), 42.07 (d), 47.22 (d), 48.45 (d), 65.62 (d); mass spectrum *m/e* (rel intensity) 171 (4, M^+), 170 (27), 135 (56), 134 (100), 121 (56), 119 (15), 105 (19), 93 (39), 92 (31), 91 (47), 79 (50), 77 (37), 67 (41).

Anal. Calcd for $C_{10}H_{15}Cl$: C, 70.38; H, 8.80; Cl, 20.82. Found: C, 70.55; H, 8.97; Cl, 20.4.

A sample (2.0 g, 0.012 mol) of the chloride was allowed to react with 0.29 g (0.012 mol) of magnesium in 10 mL of ether, and carbon dioxide was bubbled through the mixture for 2 h at ambient temperature. The crude product was purified by extraction with 5% sodium hydroxide solution, followed by acidification with concentrated hydrochloric acid, and recrystallized from methanol–water to give 0.96 g (46% yield) of pure 4-homobrendane-*exo*-2-carboxylic acid (**14**): mp 63–64 °C (sealed tube); IR (Nujol) 1700, 1310, 1295, 1260, 1230, 940, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.8 (m, 15 H), 11.7 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ_C 14.61 (t), 26.24 (t), 26.83 (t), 33.20 (t and d), 39.17 (d), 39.82 (t), 41.51 (t and t), 49.83 (d), 182.89 (s).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.19; H, 8.91.

Decarboxylation of 0.2 g (0.0011 mol) of the acid **14** with 1.2 g (0.0027 mol) of lead tetraacetate and 1.4 g (0.014 mol) of potassium acetate in 15 mL of acetic acid at reflux for 2 h gave 0.12 g (57% yield) of *exo*-2-acetoxy-4-homobrendane (**12**), which was identical in all respects with an authentic specimen of **12**.[2a]

4-Homobrend-*exo*-2-ylcarbinol (9x). The *exo*-2-carboxylic acid **14** (0.60 g, 0.0033 mol) was reduced by 0.60 g (0.016 mol) of lithium aluminum hydride in 20 mL of ether. The crude product was purified by column chromatography to give 0.53 g (96% yield) of pure 4-homobrend-*exo*-2-ylcarbinol (**9x**): IR (neat) 3300, 1050, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–2.2 (m, 15 H), 2.67 (s, 1 H), 3.30 (d, J = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ_C 15.06 (t), 26.51 (t), 27.16 (t), 33.58 (t and d), 38.33 (t), 38.45 (d), 39.30 (d), 41.70 (d), 48.32 (d), 66.43 (t); mass spectrum *m/e* (rel intensity) 166 (4, M^+), 148 (43), 136 (21), 135 (100), 119 (13), 107 (14), 94 (14), 93 (33), 91 (24), 81 (26), 79 (45), 77 (22), 67 (46).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.58; H, 10.99.

***exo*-2-Methyl-4-homobrendane (10x).** The exo carbinol **9x** (0.35 g, 0.0021 mol) was tosylated with 0.52 g (0.0028 mol) of *p*-toluenesulfonyl chloride in 10 mL of pyridine. The crude tosylate was recrystallized from ether–*n*-hexane to give 0.51 g (76% yield) of a pure sample: mp 59–60 °C; IR (neat) 1350, 1200, 1180 cm^{-1}; ^1H NMR

($CDCl_3$) δ 1.0–2.0 (m, 15 H), 2.40 (s, 3 H), 3.76 (d, J = 7 Hz, 2 H), 7.1–7.8 (m, 4 H).

Anal. Calcd for $C_{18}H_{24}O_3S$: C, 67.48; H, 7.55; S, 9.99. Found: C, 67.71; H, 7.35; S, 10.3.

The tosylate was reduced with 0.20 g (0.0052 mol) of lithium aluminum hydride in 20 mL of ether. Purification of the crude product by column chromatography gave 0.15 g (63% yield) of pure *exo*-2-methyl-4-homobrendane (**10x**): ^1H NMR ($CDCl_3$) δ 0.9–1.8 (m); ^{13}C NMR ($CDCl_3$) δ_C 15.17 (t), 21.63 (q), 26.11 (t), 27.38 (t), 33.16 (d), 33.81 (t), 38.07 (t), 39.88 (d), 42.46 (d), 44.05 (d), 44.11 (d); mass spectrum *m/e* (rel intensity) 150 (100, M^+), 135 (58), 121 (51), 109 (27), 108 (33), 107 (18), 95 (56), 94 (48), 93 (31), 81 (33).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.70; H, 12.22.

Registry No.—**1**, 49700-65-4; **2**, 66085-39-0; **3**, 66085-40-3; **4**, 66085-41-4; **5**, 66085-42-5; **6**, 16489-35-3; **7**, 50529-80-1; **8**, 66085-43-6; **9n**, 66085-44-7; **9n** tosylate, 66085-45-8; **9x**, 66140-51-0; **9x** tosylate, 66140-52-1; **10n**, 66085-46-9; **10x**, 66140-53-2; **11**, 66085-47-0; **12**, 61559-34-0; **13**, 50529-94-7; **14**, 66085-48-1; **15**, 43000-53-9; **16**, 51027-87-3; 2-Me-Ad, 700-56-1; 1-Me-Ad, 768-91-2; 2-chloro-4-homobrendane, 66085-49-2; homoadamantane, 281-46-9; *endo*-2,8-trimethylenebicyclo[3.3.0]octane, 28099-09-4.

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Metal Ion Oxidation. 6.[1] Oxidative Acetoxylation of Aromatic Compounds by Silver(II) Complexes in Acetic Acid[2]

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Received January 23, 1978

Silver(II) complexes with nitrogen-containing ligands oxidize aromatic compounds (anisole, substituted anisoles, biphenyl, naphthalene, and hexamethylbenzene) in 0.5 M KOAc/HOAc yielding acetoxy derivatives (nuclear or side-chain acetates). Anisole and biphenyl give mainly ortho and para acetates. Results from the competitive oxidation of 4-substituted anisoles gave a Hammett ρ value of -3.4. Nuclear substitution did not show any deuterium isotope effect, whereas side-chain substitution of 4-methoxytoluene gave a k_H/k_D value of 5.9. Oxidation of benzene in trifluoroacetic acid gave phenol after hydrolysis of the reaction product. It is suggested that silver(II) reacts by removing one electron from the aromatic substrate, yielding a radical cation in the initial step. The synthetic utility of the reaction is demonstrated in a catalytic process using either presynthesized bis(2,2′-bipyridine)silver(II) peroxodisulfate or a mixture of silver(I) acetate and 2,2′-bipyridine in the presence of excess potassium peroxodisulfate. Acetates are produced with catalyst efficiencies between 1500 and almost 10 000%.

Although Ag(II) is a very strong oxidant[3] its use as a reagent in organic synthesis has been limited. The oxide, AgO, and the bis(2-pyridine carboxylate), $Ag(pic)_2$, are known to oxidize a variety of organic compounds in aqueous acidic or basic media.[4] More recently it has been shown that AgO dissolved in trifluoroacetic acid (TFA) could affect oxidation of aliphatic hydrocarbons[5] and coupling of phenolic substrates.[6] Kinetic studies have been reported on the oxidation of carboxylic acids by Ag(II)[7-9] or by Ag(I) and peroxodisulfate anion, $S_2O_8^{2-}$.[10] In the latter study it was shown that Ag(II), obtained by the action of $S_2O_8^{2-}$ on Ag(I), was the primary oxidant.

In a preliminary report we described the reaction between some aromatic compounds and bis(2,2′-bipyridine)silver(II) peroxodisulfate, $Ag(bpy)_2S_2O_8$, in acetic acid containing sodium acetate.[11] The major products were arenes acetoxylated in nuclear and/or side-chain (α) positions. Methyl-substituted arenes also gave benzaldehydes. The stoichiometry of the reaction seemed to follow eq 1.

$$3ArH + 2Ag(II) + 2S_2O_8^{2-} + 3OAc^- \rightarrow 3ArOAc + 2Ag(I) + 4SO_4^{2-} + 3H^+ \quad (1)$$

As an example, 4-methoxytoluene was converted into a mixture of 4-methoxybenzyl acetate and 4-methoxybenzaldehyde in a yield of almost 300% based on Ag(II)[12] by $Ag(bpy)_2S_2O_8$. This indicated that Ag(II) as well as $S_2O_8^{2-}$ were involved in the overall reaction. The removal of one electron from the

0022-3263/78/1943-2613$01.00/0