The Reaction of 2,4-Dehydrohomoadamantane: The Synthesis of Several 2-Mono- and 2,4-Di-substituted Homoadamantanes[1)]

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The synthesis of several 2-mono- and 2,4-di-substituted homoadamantane derivatives is described. The photobromination of 2,4-dehydrohomoadamantane (I) at −78 °C gave *e,a-* and *e,e*-2,4-dibromohomoadamantanes (IIa and IIb). The treatment of a mixture of IIa and IIb with *t*-BuOK in HMPT gave *e*-2-bromohomoadamant-4-ene (IV) in an 84% yield. The methanolysis and hydrolysis of IV gave *e*-2-methoxyhomoadamant-4-ene (V) and *e*-2-hydroxyhomoadamant-4-ene (VI), with a retention of the configuration, in 90 and 99% yields respectively. The oxidation of VI with the CrO_3–pyridine complex gave homoadamant-4-en-2-one (VII) in a 94% yield. The reduction of VII with $LiAlH_4$ gave *a*-2-hydroxyhomoadamant-4-ene (VIII). The catalytic hydrogenations of VI, VII, and VIII gave *e*-2-hydroxyhomoadamantane (IX), homoadamantan-2-one (X), and *a*-2-hydroxyhomoadamantane (XI) respectively. The possibility that a homoallylic cation (XII) intervenes in the solvolysis of IV is proposed.

A large number of bridgehead-substituted (1- or 3-) homoadamantane derivatives (*cf.* Fig. 1) have been extensively studied.[2)] However, relatively speaking, there has been a remarkable absence from the chemical literature of references to the synthesis of bridge-substituted homoadamantane derivatives. Moreover, the few synthesized compounds have been restricted to those substituted only on the ethylene bridge (4- and/or 5-positions).[3)]

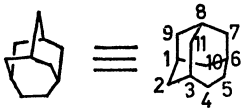
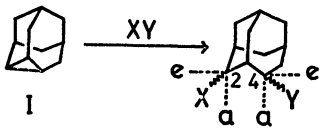


Fig. 1. Homoadamantane.

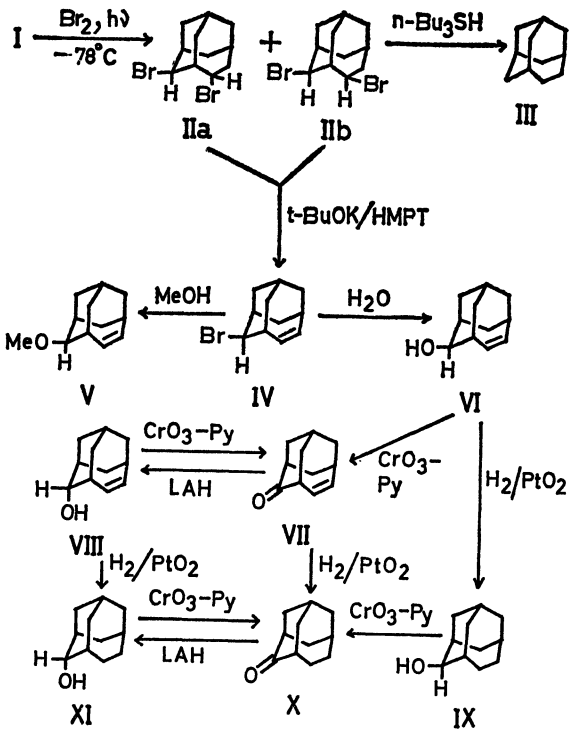
On the other hand, in the case of the adamantane system a good many bridge-substituted derivatives have been synthesized and studied.[2)] Particularly Udding *et al.* reported a very subtle synthesis of 2-mono- and 2,4-di-substituted adamantane derivatives by cleaving the cyclopropane ring of 2,4-dehydroadamantane with a variety of electrophilic reagents.[4)] We have ourselves previously reported the efficient synthesis of 2,4-dehydrohomoadamantane (I),[5)] a homologue of 2,4-dehydroadamantane. As a matter of cource, I might be a potential precursor of 2-mono- and 2,4-di-substituted homoadamantane derivatives. However, in comparison with the adamantane system there remain some difficulties; for example, an increase of one methylene carbon diminishes the high symmetry inherent to the adamantane system, causing a complex situation in the configurations of substituents in the homoadamantane system. In this paper we wish to report the first synthesis of several 2-mono- and 2,4-di-substituted homoadamantanes. The configurations of the substituents are tentatively named, as is shown in Scheme 1, after adamantane derivatives.[4)]



Scheme 1.

Results and Discussion

For cleaving the cyclopropane ring of I, we have chosen a radical-type reaction, *i.e.*, photobromination, taking account of the fact that an ionic reaction causes a skeletal alteration.[6)] Shea and Skell reported detailed studies of the photobromination of alkylcyclopropanes;[7)] we followed their procedures. When a solution of I and bromine in dichloromethane was irradiated at −78 °C for 5 min, a cleavage of the cyclopropane ring was observed, giving two dibromides (IIa and IIb, 52 : 48 by glc analysis) in an 82% yield, along with a small amount of monobromide. The structures of IIa and IIb were deduced to be 2,4-dibromohomoadamantanes on the basis of the following experimental results: (i) The reduction of IIa and IIb by tri-*n*-butyltin hydride gave homoadamantane (III), proving



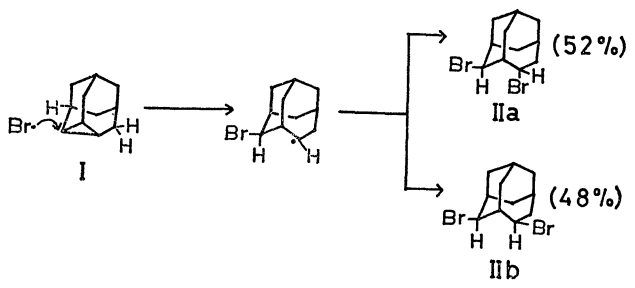
Scheme 2.

that IIa and IIb possess a homoadamantane skeleton. (ii) The treatment of IIa and IIb with a base could easily cause the elimination of one equivalent of hydrogen bromide to a sole compound (IV) (*vide infra*), indicating that one of the two bromine atoms is located on the ethylene bridge, and the other, on the methylene bridge.[8] (iii) As will be described later, the reaction of IV as well as the UV spectrum of homoadamant-4-en-2-one (VII) show that the substituents are obviously located at the 2- and 4-positions.

The treatment of a mixture of IIa and IIb with potassium *tert*-butoxide in hexamethylphosphoric triamide (HMPT) at 85—90 °C for 3 hr gave a sole product, 2-bromohomoadamant-4-ene (IV), in 80—90% yield. The above results indicate that the configuration of the bromine atom on the C-2 of IIa is identical with that of IIb. The PMR spectra of IIa, IIb, and IV are depicted in Fig. 2. As is shown in Fig. 2(c), the proton on the C-2 of IV does not couple with the adjacent bridge-head protons on the C-1 and C-3. The PMR studies using a shift reagent on 3-homoadamantanol established that the axial proton on the C-2 does not couple with the adjacent bridge-head proton, while the equatorial one does couple with the adjacent one, with a coupling constant of 4 Hz.[9] This report as well as the model investigation (FMM model) indicate that the proton on the C-2 must have the axial orientation. Thus, the structure of IV can be determined to be *e*-2-bromohomoadamant-4-ene.

The configurations at the C-4 positions of IIa and IIb were determined as follows. The difference between the chemical shift of the proton on the C-2 and that on the C-4 in IIa is larger than that in IIb, as is shown in Fig. 2(a) and 2(b). By analogy with the results for 2,4-dibromoadamantane,[10] we can deduce that IIa is *e,a*-2,4-dibromohomoadamantane and that IIb is *e,e*-2,4-dibromohomoadamantane.

The fact that the photobromination of I gives no *a,a*-2,4-dibromohomoadamantane is considered to be very similar to the case of 2,4-dehydroadamantane reported by Shea and Skell.[7,11] According to the mechanism suggested by them, the photobromination of I can proceed through the sequences shown in Scheme 3. It is of interest to note that the initial attack on the cyclopropane ring by the bromine atom is effected from the six-membered-ring side selectively. A larger steric requirement of the methylene hydrogen atoms on the C-5 than that of the methine hydrogen atom on the C-1 would inhibit the attack of the bromine atom from the seven-membered-ring side.



Scheme 3.

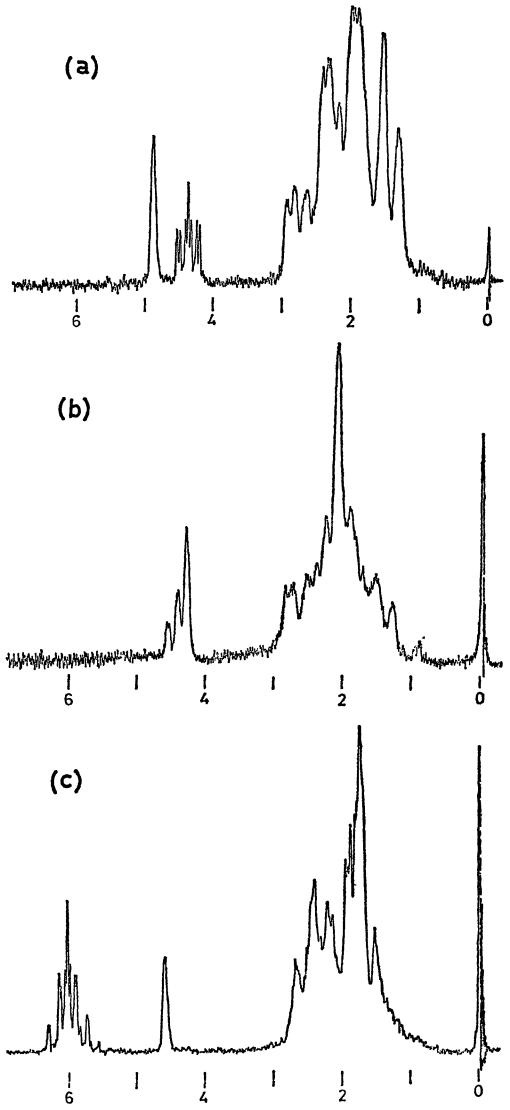


Fig. 2. PMR spectra of IIa, IIb, and IV.
(a): IIa, (b): IIb, and (c): IV.

The treatment of IV with methanol gave *e*-2-methoxyhomoadamant-4-ene (V) in a 90% yield, with a retention of the configuration. The configuration at the C-2 position of V was determined by PMR analysis in analogy with that of IV (see Experimental Section). When IV was hydrolyzed in 25% aqueous dioxane at the reflux temperature for 2 hr, *e*-2-hydroxyhomoadamant-4-ene (VI) was obtained in a 99% yield, again with a complete retention of the configuration. The oxidation of VI with a chromic anhydride–pyridine complex in dichloromethane gave homoadamant-4-en-2-one (VII) in a 94% yield. The UV spectrum of VII showed an n-π^* absorption at 300 nm (ε=127) (in EtOH); this suggests a homoconjugation between the carbonyl and the olefinic moieties.[12] The reduction of VII with lithium aluminum hydride in ether or sodium borohydride in ethanol gave *a*-2-hydroxyhomoadamant-4-ene (VIII) predominantly, along with a small amount of VI (VIII : VI=96 : 4 in the case of lithium aluminum hydride and 94 : 6 in the case of sodium borohydride, as determined by glc analysis). The PMR spectrum of VIII, shown in Fig. 3 (b),

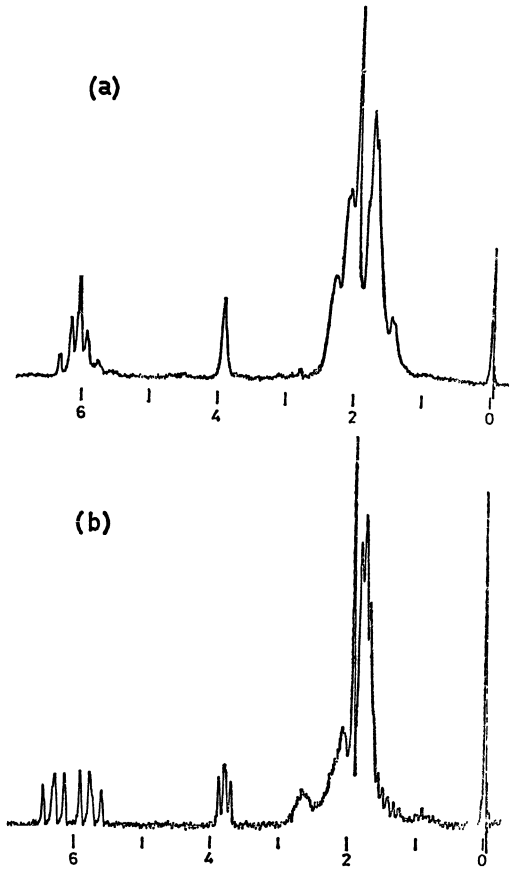
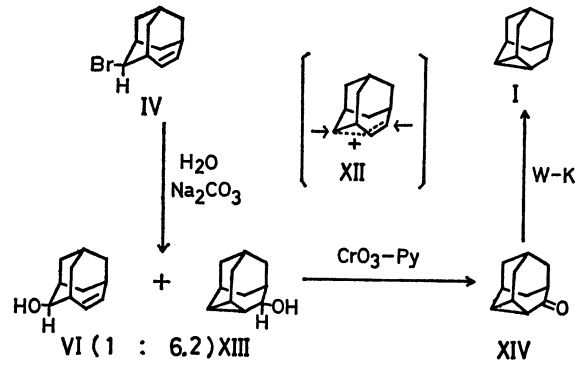


Fig. 3. PMR spectra of VI and VIII.
(a): VI, (b): VIII.

indicates that equatorial proton on the C-2 couples with the adjacent bridge-head protons with a coupling constant of *ca.* 4 Hz. The oxidation of VIII with a chromic anhydride–pyridine complex caused VIII to revert to VII, showing that no skeletal rearrangement took place during the above transformations.

The catalytic hydrogenations of VI, VII, and VIII utilizing platinum oxide in ethyl acetate gave the corresponding saturated compounds, *e*-2-hydroxyhomoadamantane (IX), homoadamantan-2-one (X), and *a*-2-hydroxyhomoadamantane (XI), in 98, 88, and 90% yields respectively. The oxidation of IX gave X. The reduction of X with lithium aluminum hydride in ether gave XI exclusively. The high stereoselectivities observed in the reductions of X as well as VII (*vide supra*) are similar to that observed in the reduction of bicyclo[3.3.1]nonan-2-one.[13] Moreover, it was confirmed that the Wolff-Kishner reduction of X gave the parent system, III. Thus, the above-mentioned transformations, depicted in Scheme 2, unequivocally confirm the structures of 2-mono- and 2,4-di-substituted homoadamantanes.

The complete retention of configuration at the C-2 position observed in the solvolysis of IV suggests the intervention of a homoallylic cation (XII).[14] In order to verify this possibility, we have solvolyzed IV in the presence of a buffer. When IV was hydrolyzed in 25% aqueous dioxane in the presence of sodium carbonate or potassium hydroxide, a new alcohol (XIII) was produced, along with a small amount of VI (XIII : VI=*ca.* 6 : 1 by glc analysis) (Scheme 4). The structure of XIII was deduced to be *e*-5-hydroxy-2,4-dehydrohomoadamantane on the basis of the following chemical and spectroscopic results: (i) The PMR spectrum of XIII had no signal due to the olefinic proton. (ii) The oxidation of XIII with the chromic anhydride–pyridine complex gave 2,4-dehydrohomoadamantane-5-one (XIV), which was then reduced by the Wolff-Kishner method to give I. (iii) A model investigation (FMM model) tells us that the axial proton on the C-5 of XIII must couple with the adjacent bridge-head protons, while the equatorial one does not, because the dihedral angle is nearly 90°. Since the PMR spectrum of XIII shows that the proton on the C-5 copules with the adjacent bridge-head protons with the coupling constant of *ca.* 6 Hz, XIII is determined to be *e*-5-hydroxy-2,4-dehydrohomoadamantane.



Scheme 4.

A complete understanding could, of course, be obtained by further precise experiments. However, the present results give powerful support to the notion that a homoallylic cation (XII) plays an important role in the solvolysis of IV.

Experimental

All the temperatures are uncorrected. The melting points were measured in a sealed tube in a liquid bath. The IR spectra were obtained on a Shimadzu IR-27 spectrometer. The UV spectra were recorded on a Hitachi EPS-2 spectrophotometer. The MS spectra were taken by using a Hitachi RMS-4 mass spectrometer. The PMR spectra were obtained on a Varian EM-360 spectrometer, TMS being chosen as the internal standard. The microanalyses were performed by Mrs. Kiyoko Fujimoto. No attempt has been made to maximize the yields of the reactions reported below.

2,4-Dihydrohomoadamantane (I). This compound was synthesized by the previously reported method.[5] A small contamination of homoadamant-4-ene can be easily removed by the treatment of the crude mixture with an appropriate amount of bromine in CH_2Cl_2, followed by column chromatography on silica gel eluted with *n*-hexane.

e,a-*2,4-Dibromohomoadamantane (IIa) and* e,e-*2,4-Dibromohomoadamantane (IIb).* A solution of I (1605 mg; 10.8 mmol) and Br_2 (0.54 ml, 1685 mg; 10.4 mmol) in 180 ml of CH_2Cl_2 was irradiated by means of a 300W medium-pressure mercury arc (soft glass filter) at −78 °C for 5 min. The reaction mixture was then warmed up to room temperature, washed successively with 10% aq. Na_2SO_3, aq. $NaHCO_3$, and brine, and dried (Na_2SO_4). The solvent was then

removed, and the residue (3008 mg) was chromatographed on silica gel (200 g). Elution by *n*-hexane gave first the unreacted starting material (208 mg) and then a monobromide of an unknown structure. Further elution by *n*-hexane gave IIa (187 mg), a mixture of IIa and IIb (2007 mg), and IIb (170 mg). The total yield of the dibromides, IIa and IIb (2364 mg), was 81.5%, calculated on the basis of the reacted I. The ratio of IIa to IIb was determined by glc analysis to be 52 : 48 (HVSG, 130 °C). IIa: mp 121—124 °C; IR (Nujol) 2950, 1460, 1380, 795, 720 cm^{-1}; PMR δ (CCl_4) 1.13—3.05 (broad complex m, 14H), 4.36 (d.d.d, 1H, J=2.8, 7.0, and 9.8 Hz), 4.89 (broad s, 1H); Found: C, 42.61; H, 5.26%. Calcd for $C_{11}H_{16}Br_2$: C, 42.88; H, 5.24%. IIb: mp 55—58 °C; IR (Nujol) 2950, 1460, 1380, 730 cm^{-1}; PMR δ (CCl_4) 1.07—3.05 (broad complex m, 14H), 4.41 (m, 2H); Found: C, 42.70; H, 5.27%. Calcd for $C_{11}H_{16}Br_2$: C, 42.88; H, 5.24%.

A mixture of IIa and IIb (115 mg; 0.37 mmol), *n*-Bu_3SnH (441 mg; 1.5 mmol), and benzene (2 ml) was refluxed under N_2 for 3 hr. The reaction mixture was then washed with brine and dried (Na_2SO_4). After the solvent had subsequently been removed, the residue was shown by glc analysis (PEG 20 M, 16 °C) to contain only one compound as a hydrocarbon component. This compound was isolated by preparative glc and determined to be homoadamantane (III) by comparison with the authentic sample [3b] (glc retention time, and MS and PMR spectra).

e-*2-Bromohomoadamant-4-ene (IV).* A solution of IIa and IIb (1668 mg; 5.42 mmol) and *t*-BuOK (705 mg; 6.29 mmol) in 17 ml of HMPT was heated at 85—88 °C for 3.5 hr under a nitrogen atmosphere. To the cooled reaction mixture we then added *n*-hexane, and the organic layer was repeatedly washed with brine and dried (Na_2SO_4). The solvent was then evaporated under reduced pressure, and the residue was sublimed (100—105 °C/10 mmHg) to give pure IV (1035 mg, 84.2%): mp 92—96 °C; MS: *m/e* 228 and 226 (M^+, 23 and 24%), 147 (100%); IR (Nujol) 2950, 1660 (weak), 1460, 1380, 1175, 790, 730, 695 cm^{-1}; PMR δ(CCl_4) 1.20—3.00 (broad complex m, 12H), 4.63 (broad s, 1H), 6.07 (m, 2H); Found: C, 58.40; H, 6.85%. Calcd for $C_{11}H_{15}Br$: C, 58.16; H, 6.66%.

The same treatment of pure IIa (126 mg; 0.41 mmol) with *t*-BuOK (74 mg; 0.66 mmol) in HMPT (3 ml) gave IV (82 mg, 88%).

The reaction was very sensitive to the reaction temperature, since IV was not very stable. When the temperature was higher, the resulting IV was converted to another compound, the structure of which was unknown. In our experiments, the yields were between 80 and 90%.

e-*2-Methoxyhomoadamant-4-ene (V).* A solution of IV (45 mg; 0.2 mmol) in 1 ml of methanol was heated at reflux for 5 hr. The reaction mixture was then concentrated under reduced pressure, and the residue was chromatographed on silica gel. Elution by *n*-hexane gave V (32 mg, 90%): bp 101—104 °C/22 mmHg; MS:*m/e* 178 (M^+, 100%); IR (neat) 2950, 1660 (weak), 1450, 1380, 1190, 1090, 945, 885, 735, 715 cm^{-1}; PMR δ (CCl_4) 1.10—2.57 (broad complex m, 12H) 3.20 (broad s, 1H), 3.26 (s, 3H), 6.00 (m, 2H); Found: C, 80.72; H, 10.39%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%.

e-*2-Hydroxyhomoadamant-4-ene (VI).* A solution of IV (449 mg; 1.98 mmol) in 20 ml of 25% aq. dioxane was heated at reflux for 2 hr. To the reaction mixture we then added aqueous $NaHCO_3$, and an organic material was extracted with CH_2Cl_2. The solution was washed with brine and dried (Na_2SO_4). The solvent was removed to give crude VI (322 mg, 99%): mp (from *n*-hexane) 226—229 °C; MS: *m/e* 164 (M^+, 96%), 91 (97%), 79 (100%); IR (Nujol) 3300, 2950, 1650 (weak), 1460, 1380, 1025, 710 cm^{-1}; PMR δ ($CDCl_3$) 1.10—2.70 (broad complex m, 12H), 2.01 (s, 1H, OH), 3.93 (broad s, 1H), 6.05 (m, 2H); Found: C, 80.34; H, 9.96%. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83%.

Homoadamant-4-en-2-one (VII). To a solution of pyridine (2.5 ml) in 12 ml of CH_2Cl_2, we gradually added CrO_3 (520 mg; 5.2 mmol). The solution was stirred at room temperature for 5 min, and then, to this solution, we added, drop by drop, a solution of VI (99 mg; 0.6 mmol) in 3.5 ml of CH_2Cl_2. The reaction mixture was stirred at room temperature for 2 hr and then washed successively 5% aqueous NaOH saturated with NaCl, 5% aqueous HCl (twice), aqueous $NaHCO_3$, and brine. The organic layer was dried (Na_2SO_4) and passed through a short alumina column. The solvent was removed to give crude VII (92 mg, 94%): mp (from *n*-hexane) 244—248 °C; MS: *m/e* 162 (M^+, 100%); IR (Nujol) 2950, 1710, 1650 (shoulder), 1460, 1380, 710 cm^{-1}; UV λ_{max} (EtOH) 300 nm (ε=127); PMR δ ($CDCl_3$) 1.63—3.23 (broad complex m, 12H), 6.10 (m, 2H); Found: C, 81.35; H, 8.88%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

a-*2-Hydroxyhomoadamant-4-ene (VIII).* To a suspention of $LiAlH_4$ (134 mg) in 10 ml of dry ether, we added, drop by drop, a solution of VII (120 mg; 0.74 mmol) in 10 ml of dry ether. The reaction mixture was then stirred at reflux temperature overnight. The usual work-up[15] and the removal of the solvent gave crude VIII, along with a small amount of VI (119 mg, 98%, VIII : VI=96 : 4 by glc analysis (PEG 20 M, 180 °C)). The crude material was chromatographed on alumina. Elution by a mixture of *n*-hexane and CH_2Cl_2 (7 : 3) gave pure VIII: mp 282—284 °C; MS: *m/e* 164 (M^+, 100%); IR (Nujol) 3300, 2950, 1665 (weak), 1460, 1380, 1060, 1040 cm^{-1}; PMR δ ($CDCl_3$) 1.20—2.90 (broad complex m, 12H), 1.92 (s, 1H, OH), 3.80 (d.d, 1H, J=4 and 4 Hz), 6.00 (m, 2H); Found: C, 80.25; H, 9.99%. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83%.

To a solution of VII (62 mg; 0.38 mmol) in 2 ml of EtOH, we added $NaBH_4$ (32 mg; 0.84 mmol), portion by portion, in an ice-bath. The reaction mixture was stirred at room temperature for 15 min, poured into water, and extracted with ether. The extract was washed with brine and dried (Na_2SO_4). The solvent was removed to give a crude product (59 mg, 93%; VIII : VI=94 : 6 by glc analysis).

The oxidation of VIII with the CrO_3-pyridine complex by the use of the procedure described above gave the starting material, VII, in a 97% yield.

e-*2-Hydroxyhomoadamantane (IX).* A solution of VI (32 mg; 0.2 mmol) and a small amount of PtO_2 in 2 ml of EtOAc was vigorously stirred under a hydrogen atmosphere. After 1 equivalent of H_2 had been absorbed, the PtO_2 was removed by filtration and the filtrate was evaporated under reduced pressure to give crude IX (31 mg, 98%): mp (from *n*-hexane) 257—260 °C; MS: *m/e* 148 (100%); IR (Nujol) 3300, 2950, 1460, 1380, 1030 cm^{-1}; PMR δ ($CDCl_3$) 1.00—2.30 (broad complex m, 16H), 2.00 (s, 1H, OH), 3.60 (broad s, 1H); Found: C, 79.27; H, 11.15%. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92%.

Homoadamantan-2-one (X). The procedure was essentially the same as that described above. The VII compound (102 mg; 0.63 mmol) gave X (92 mg, 88%): mp (from petroleum ether) 260—263 °C; MS: *m/e* 164 (M^+, 100%); IR (Nujol) 2950, 1720, 1460, 1380 cm^{-1}; PMR δ($CDCl_3$) 1.07—2.80 (broad complex m, 16H); Found: C, 80.24; H, 10.00%. Calcd for $C_{11}H_{16}O$: C, 80.44%; H, 9.83%.

The Wolff-Kishner reduction of X was conducted by the

use of the procedure described for the reduction of 2,4-dehydrohomoadamantan-5-one (XIV) (*vide infra*). The treatment of X (54 mg; 0.33 mmol) with KOH (368 mg) and 100% hydrazine hydrate (273 mg) in diethylene glycol (2 ml) gave homoadamantane (III) (35 mg, 71%), which was identical with an authentic sample[3b] (glc retention time, and MS and PMR spectra).

a-2-*Hydroxyhomoadamantane (XI).* This compound was prepared similarly from VIII in a 90% yield: mp (from *n*-hexane) >290 °C; MS: *m/e* 148 (100%); IR (Nujol) 3300, 2950, 1460, 1380, 1060, 1015 cm^{-1}; PMR $\delta(CDCl_3)$ 1.11—2.50 (broad complex m, 16H), 1.73 (s, 1H, OH), 3.83 (d.d, 1H, J=5 and 3.5 Hz); Found: C, 79.22; H, 11.13%. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92.

To oxidation of IX or XI by the CrO_3-pyridine complex gave a ketone, X. The reduction of X with $LiAlH_4$ in ether gave exclusively the axial epimer (XI). A PMR study showed the absence of IX.

e-*5-Hydroxy-2,4-dehydrohomoadamantane (XIII).* A solution of IV (322 mg; 1.4 mmol) and Na_2CO_3 (278 mg) in 10 ml of 25% aqueous dioxane was heated at reflux for 3 hr. The reaction mixture was then cooled, poured into water, and extracted with CH_2Cl_2. The extract was washed with brine and dried (Na_2SO_4). The subsequent removal of the solvent gave crude products (220 mg, 98%) which contained VI and XIII (1 : 6.2 by glc analysis; PEG 20 M, 160 °C). The separation of VI and XIII was effected by column chromatography on silica gel. Elution by *n*-hexane and ether (95 : 5) gave pure XIII (97 mg) and, subsequently, a mixture of VI and XIII (121 mg). The properties of XIII were as follows: mp (from *n*-hexane) 264—265 °C; MS: *m/e* 164 (M^+, 26%), 146 (100%); IR (Nujol) 3300, 2950, 1460, 1380, 1035 cm^{-1}; PMR $\delta(CDCl_3)$ 0.67—2.33 (broad complex m, 14H), 1.67 (s, 1H, OH), 4.40 (t, 1H, J=6 Hz); Found: C, 80.59; H, 9.98%. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83%.

When KOH was used in place of Na_2CO_3, the same products were obtained (VI : VIII = 1 : 6.9). When $AgClO_4$ was used, the reaction proceeded at room temperature but the product distribution was almost the same as has been described above (VI : XIII = 1 : 7.2).

2,4-*Dehydrohomoadamantan*-5-*one (XIV).* To a solution of pyridine (1.5 ml) in 7 ml of CH_2Cl_2, we gradually added CrO_3 (267 mg; 2.7 mmol). The solution was stirred at room temperature for 5 min, and then to this solution we added a solution of XIII (50 mg; 0.3 mmol) in 2 ml of CH_2Cl_2. The reaction mixture was stirred at room temperature for 2 hr and washed successively with 5% aqueous NaOH saturated with NaCl, 5% aqueous HCl (two times), 5% aqueous NaOH, and brine. The organic layer was dried (Na_2SO_4) and passed through a short alumina column. The solvent was removed to give crude XIV (44 mg, 90%): mp (from *n*-hexane) 238—241 °C; MS: *m/e* 162 (M^+, 100%); IR (Nujol) 2950, 1710, 1460, 1380 cm^{-1}; PMR $\delta(CDCl_3)$ 0.70—2.57 (broad complex m, 14H); Found: C, 81.38; H, 8.88%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

The Wolff-Kishner reduction of XIV was conducted following the procedure reported for the reduction of 8,9-dehydro-2-adamantanone.[16] A solution of XIV (31 mg; 0.19 mmol), KOH (208 mg), and 100% hydrazin hydrate (153 mg) in 1 ml of diethylene glycol was stirred at 110 °C for 30 min and subsequently at 180 °C for 3 hr. The material sublimed on the condenser was dissolved in petroleum ether (40—60 °C) and dried (Na_2SO_4). The subsequent removal of the solvent gave a sole product (21 mg, 75%), which was confirmed to be I by comparison with an authentic specimen (glc retention time, and MS and PMR spectra).

The UV maximum in $CHCl_3$ at 380 nm for the 2,4-dinitrophenylhydrazone of XIV was appropriate for a conjugated carbonyl function in comparison with the UV maximum in $CHCl_3$ at 371 nm for the 2,4-dinitrophenylhydrazone of 4-homoadamantanone.[17]

The 2,4-dinitrophenylhydrazone of XIV: mp (from EtOH) 184—185.5 °C; UV λ_{max} ($CHCl_3$) 380 nm; Found: C, 59.46; H, 5.26; N, 16.10%. Calcd for $C_{17}H_{18}O_4N_4$: C, 59.64; H, 5.30; N, 16.37%.

The 2,4-dinitrophenylhydrazone of 4-homoadamantanone: mp (from EtOH) 210—211 °C; UV λ_{max} ($CHCl_3$) 371 nm; Found: C, 59.18; H, 6.11; N, 16.36%. Calcd for $C_{17}H_{20}O_4N_4$: C, 59.29; H, 5.85; N, 16.27%.

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References

1) Throughout this paper we have adopted trivial nomenclature for simplicity. The IUPAC names for 2,4-dehydrohomoadamantane and homoadamantane are tetracyclo[5.3.1.$0^{5,3}$.$0^{4,9}$]undecane and tricyclo[4.3.1.$1^{3,8}$]undecane, respectively.

2) For pertinent references; R. C. Fort, Jr. and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); R. C. Bingham and P. v. R. Schleyer, *Fortschr. Chem. Forsch.*, **18**, 1 (1971).

3) As to the methylene-bridge-substituted compounds, there is only one report, which is concerned with 2,7-disubstituted homoadamantanes; B. R. Vogt, *Tetrahedron Lett.*, **1968**, 1575. As to the ethylene-bridge-substituted compounds, see the following reports; (a) D. R. Kell and F. J. McQuillin, *Chem. Commun.*, **1970**, 599; K. Bott, *ibid.*, 1349 (1969); D. R. Kell and F. J. McQuilline, *J. Chem. Soc., Perkin Trans. I*, **1972**, 2100; K. Bott, *Ann. Chem.*, **766**, 51 (1972). (b) J. E. Nordlander, F. Y.-H. Wu, S. P. Jindal, and J. B. Hamilton, *J. Amer. Chem. Soc.*, **91**, 3962 (1969); P. v. R. Schleyer, E. Funke, and S. H. Liggero, *ibid.*, **91**, 3965 (1969). (c) I. Tabushi, Z. Yoshida, and N. Takahashi, *ibid.*, **92**, 6670 (1970); R. M. Black and G. B. Gill, *J. Chem. Soc., C*, **1970**, 671; J. L. M. A. Schlatmann, J. G. Korsloot, and J. Schut, *Tetrahedron*, **26**, 949 (1970); E. Bernaert, D. Danneels, M. Anteunis, and G. Verhegge, *ibid.*, **29**, 4127 (1973).

4) A. C. Udding, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, **1968**, 1345.

5) The first synthesis; Z. Majerski, S. H. Liggero, and P. v. R. Schleyer, *Chem. Commun.*, **1970**, 949. Our results; R. Yamaguchi, T. Katsushima, T. Imagawa, and M. Kawanishi, *Synthetic Commun.*, **1974**, 83; R. Yamaguchi, T. Katsushima, and M. Kawanisi, This Bulletin, **47**, 2830 (1974).

6) An investigation concerned with the ionic cleavage of I is in progress in our laboratory, and it has been found that the homoadamantane skeleton was converted to other tricycloundecane system. The details will be the subject of further report.

7) K. J. Shea and P. S. Skell, *J. Amer. Chem. Soc.*, **95**, 6728 (1973).

8) According to the Bredt rule, it is highly probable that the bromine atom which locates on the methylene-bridge can not be eliminated to give an olefin. For example see E. Cuthbertson and D. D. MacNicol, *Tetrahedron Lett.*, **1974**, 2367.

9) H. Langhals and C. Rüchardt., *Chem. Ber.*, **107**, 1245 (1974).

10) F. W. v. Deursen and J. Bakker, *Tetrahedron*, **27**, 4593

(1971).

11) The ratio of *e,a*- and *e,e*-derivative in the photobromination of I was different from that of 2,4-dehydroadamantane (*e,a*-: *e,e*-=66 : 34).

12) For homoconjugation, see L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Princeton, N. J. (1963), p. 441 and 525.

13) (a) K. H. Baggaley, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, **23**, 299 (1967). (b) J. P. Schaefer, J. C. Lark, C. A. Flegal, and L. M. Honig, *J. Org. Chem.*, **32**, 1732 (1967).

14) Review: B. Capon, *Quart. Rev.*, **18**, 45 (1964); M. Hanack and H. J. Schneider, *Angew. Chem. Int. Ed. Engl.*, **6**, 666 (1967); H. G. Richey, "Carbonium Ions," Vol. 3, ed. by G. A. Olah and P. v. R. Schleyer, Wiley-Interscience, New York, N. Y. (1972), Chapter 25.

15) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, John Wiley & Sons, Inc., New York, N. Y. (1967). p. 581.

16) R. K. Murray, Jr. and K. A. Baliak, *J. Org. Chem.*, **38**, 2556 (1973).

17) J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4303 (1968).