BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (11), 2830—2835 (1974)

The Synthesis of 2,4-Dehydrohomoadamantane[1)]

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(Received April 26, 1974)

A synthesis of 2,4-dehydrohomoadamantane (I) is described. a) The UV irradiation of a solution of 4-homoadamantene (IV) in xylene containing a small amount of methanesulfonic acid under nitrogen gave a 2: 1 mixture of I and IV after 7 day; this mixture afforded pure I in a 40% isolation yield. b) The oxidation of 4-homoadamantyl hydrazone (XI) by Pb(OAc)$_4$, NiPO, and MnO$_2$ (active) gave a 7—11: 1 mixture of I and IV respectively. It was observed that the ratio of I to IV depends on the reaction temperature, and that the oxidation of XI by Pb(OAc)$_4$ at −78 °C gave thirty times as much I as IV. The addition of MeOH as a proton source reduced the ratio of I to IV in the cases of NiPO and MnO$_2$. The Bamford-Stevens reactions of 4-homoadamatyl tosylhydrazone (II) were effected in aprotic as well as in protic solvents. The ratio of I to IV was inverted under aprotic and protic conditions. The selectivities in the oxidation of XI and the Bamford-Stevens reactions of II were explained by considering the conformations of 4-homoadamantylidene (XII) and the 4-homoadamantyl cation (VIII).

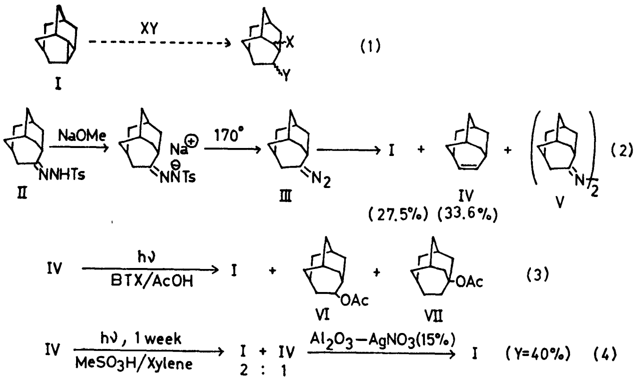
When cage compounds include a cyclopropane ring in their framework, their chemistry is intriguing in view of recent advances in the field of cyclopropane chemistry;[2)] such compounds can be adequate precursors of further substituted cage compounds. For example, 2,4-dehydroadamantane has been used in the stereochemical studies of photobromination of cyclopropanes;[3)] it is also effective as the precursor of a variety of 2- and 2,4-substituted adamantane derivatives.[4)]

Consequently, it is likely that 2,4-dehydrohomoadamantane (I) is a potential precursor of yet-unknown 2- and 2,4-substituted homoadamantane derivatives (Scheme 1, Eq. (1)). As for the synthesis of I, Schleyer *et al.* reported that the Bamford-Stevens reaction of 4-homoadamantyl tosylhydrazone (II) gave I (25.7%) and 4-homoadamantene (IV) (33.6%), along with a small amount of 4-homoadamantyl azine (V)[5)] (Scheme 1, Eq. (2)). According to their procedure, however, not only was the yield of I unsatisfactory, but also a rather larger amount of IV was produced. In this report we wish to describe a synthesis of I *via* a) a "hot" 4-homoadamantyl cation (VIII) generated photochemically and b) 4-homoadamantylidene (XII) generated by the oxidation of 4-homoadamantyl hydrazone (XI).

Results and Discussions

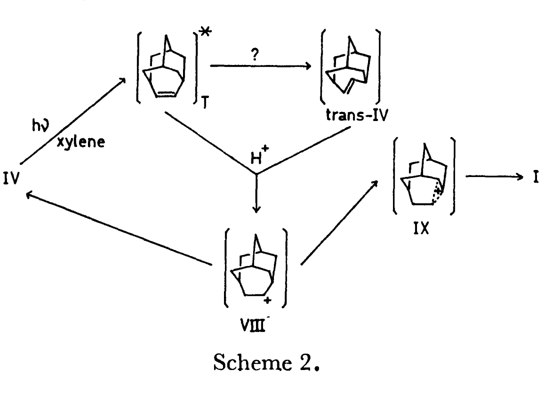
Photochemical Synthesis of I via *"Hot" (Vibrationally-excited) 4-Homoadamantyl Cation.* In a previous communication,[6)] we reported that the BTX-sensitized photochemical reaction of IV in acetic acid afforded I, along with 4- and 3-homoadamantyl acetates (VI and VII) (Scheme 1, Eq. (3)). On the other hand, there have been two reports on the acetolysis of 4-homoadamantyl tosylate giving IV and VI.[7a)] These differences can be explained by assuming a vibrationally-excited nature of the VIII formed photochemically.[7b,8)] In order to obtain I effectively, we investigated the reaction conditions under which no adducts, namely, VI and VII, were produced. Since the formation of adducts is caused by a nucleophilic attack of the protic solvent (in this case, acetic acid) on the cation before the completion of the deprotonation to produce I as well as IV, it is hoped that the use of the proton source with a poor nucleophilicity will increase the yield of I. This was to be the case when use was made of methanesulfonic acid, which has almost no nucleophilicity, as the proton source.

The UV irradiation of a solution of IV in xylene (commercial mixture) containing methanesulfonic acid under nitrogen gave a 2: 1 mixture of I and IV after 7 day; this mixture was chromatographed on a 15% AgNO$_3$–alumina column eluted by petroleum ether, giving pure I in a 40% isolation yield (Scheme 1, Eq. (4)).



Scheme 1.

Upon the replacement of methanesulfonic acid by sulfuric or hydrochloric acid as a proton source, I was not produced, presumably because of the sensitivity of the resulting I toward these acids. The addition of



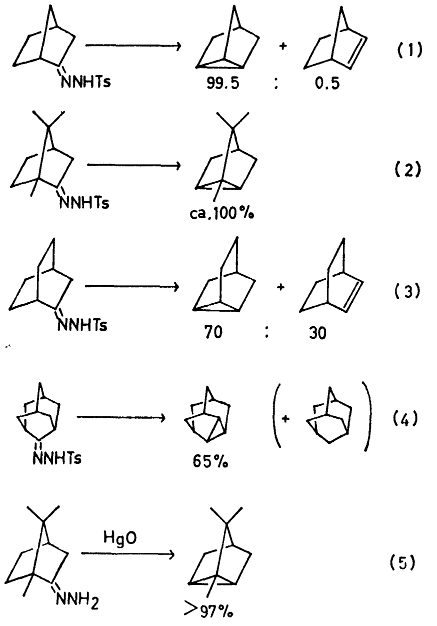
Scheme 2.

tert-butyl alcohol to increase the solubility of methanesulfonic acid (methanesulfonic acid dissolves poorly in xylene) caused only a slight isomerization to I.

The possible mechanism of the photoisomerization of IV to I is depicted in Scheme 2. Since the 4-homoadamantyl cation (VIII), produced according to the general pattern of the polar photochemistry of cycloalkenes,[8)] can be expected to be in a vibrationally-excited state, VIII must have the enhanced nature of the nonclassical cation (IX), which can be nicely deprotonated to give I.

Selective Synthesis of I by the Oxidation of 4-Homoadamantyl Hydrazone (XI). The intramolecular γ-C–H insertion of carbene intermediates is one of the most general methods of cyclopropane formation in the skeleton of cage compounds. The Bamford-Stevens reaction, the alkaline-thermolysis of tosylhydrazone, has been repeatedly used to synthesize numerous cage compounds involving cyclopropane rings.[9)] The distribution of a cyclopropane and an olefin in the resulting mixture varies according to the structure of the reactants (Scheme 3). For example, Bamford-Stevens reactions of tosylhydrazones of norcamphor and camphor gave exclusively nortricyclene and tricyclene respectively[10,11)] (Scheme 3, Eqs. (1) and (2)), but the tosylhydrazone of bicyclo[2.2.2]octan-2-one afforded tricyclo[3.2.1.0^{2,7}]-octane (70%) and bicyclo[2.2.2]oct-2-ene (30%)[12)] (Scheme 3, Eq. (3)). When the resulting olefin violates Bredt's Rule,[13)] only the cyclopropane compound was produced. For example, adamantyl tosylhydrazone gave 2,4-dehydroadamantane (65%) along with a slight amount of adamantane[14)] (Scheme 3, Eq. (4)). As mentioned above, in the homoadamantane derivative the Bamford-Stevens reaction of II gave I (27.5%) and IV (33.6%).[5)]

Friedman and Shechter successfully explained the distributions of olefins, cyclopropanes, and other transannular insertion products in Bamford-Stevens reactions of tosylhydrazones of 5- to 10-membered ring ketones by a consideration of the conformation of each carbene intermediate; they found that the distribution of the products depended on the conformations of the carbene intermediates.[15)] While in a Bamford-Stevens reaction a higher temperature (100—200 °C) is generally required to complete the decomposition of the salt of the tosylhydrazone, the conformation of the carbene intermediate generated at the higher temperature would be different from that of one generated at lower temperature. Therefore, if the corresponding carbene can be produced at a lower temperature, we can expect that the product distribution will be varied. One of the well-known methods of producing a diazoalkane, a precursor of a carbene, at a low temperature is the oxidation of the appropriate hydrazone. As an example of cyclopropane formation by the oxidation of hydrazone, the oxidation of the hydrazone of camphor by mercuric oxide is typical in giving tricyclene exclusively;[16)] this result is in good agreement with that of the Bamford-Stevens reaction, and no effect of lowering the reaction temperature was observed upon the distribution of the products in the bicyclo[2.2.1]heptane system, which is highly rigid (Scheme 3, Eq. (5)).

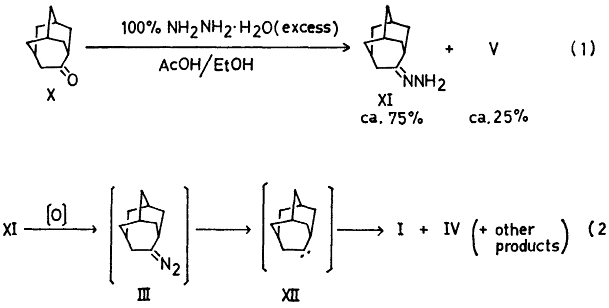


Scheme 3.

In the homoadamantane system, however, we found that the oxidation of 4-homoadamantyl hydrazone (XI) by $Pb(OAc)_4$ at room temperature gave 8 times more I than IV; this result is greatly different from that of the Bamford-Stevens reaction.[17)] In order to obtain I exclusively we studied in detail the oxidation of XI, taking the kind of oxidant and the reaction temperature as well as the catalytic effects into consideration. Finally, we will discuss the cause of the selectivity observed in the oxidation of XI in comparison with the Bamford-Stevens reactions under aprotic and protic conditions.

The hydrazone (XI) was prepared by treating 4-homoadamantanone (X) with an excess of hydrazine hydrate, along with V (20—25%) (Scheme 4). This hydrazone is considerably labile and is easily converted into V even at room temperature. Therefore, in the actual process we used the crude XI for the following oxidation immediately after it has been prepared containing an unspecified amount of V; the yields of the products were estimated on the basis of X, the starting material for XI.

Oxidants: Several oxidants were examined for the oxidation of XI (Scheme 4, Eq. (2); the results are summarized in Table 1. While mercuric oxide did not



Scheme 4.

oxidize XI, probably because of its low oxidizing ability, lead tetraacetate ($Pb(OAc)_4$), nickel peroxide (NiPO),[18] and active manganese dioxide (MnO_2)[19] all did oxidize XI. In the case of $Pb(OAc)_4$, 4-homoadamantyl acetate (VI) was produced, while in the case of NiPO as well as MnO_2, 4-homoadamantanol (XIII) and X were produced.

As is shown in Table 1, 7—11 times more I is produced than IV. Since it is thought that both reactions, the oxidation of XI and the Bamford-Stevens reaction of II, must have the same intermediate, 4-homoadamantylidene (XII) generated *via* 4-diazohomoadamantane (III), such a selectivity must result from changing the reaction conditions, especially the reaction temperature.[20] Therefore, we next studied the temperature effect.

TABLE 1. OXIDATION OF XI[a)]

Oxidant	I+IV (%)[b)]	I/IV[c)]
HgO	—	—
$Pb(OAc)_4$	37.6	8.7
NiPO	36.8	11.5
MnO_2(active)	43.5	7.2

a) One equivalent of oxidant was used in CH_2Cl_2 solution at room temp. b) Isolated yield. c) Determined by glc (PEG 20M, 180 °C).

Temperature Effect: The oxidation of XI by $Pb(OAc)_4$ was effected at a variety of temperatures. The results are summarized in Table 2.[21] Clearly, a temperature effect was observed; at −78 °C thirty times as much I was produced as IV. These temperature effects imply that some conformational contributions must operate in the transition state (*vide infra*).

TABLE 2. TEMPERATURE EFFECT IN THE OXIDATION OF XI[a)]

Temp.	I+IV (%)[b)]	I/IV[c)]	VI (%)[b)]
Room temp.	37.6	8.7	24
−15 °C	42.6	15.4	23
−30	44.8	23.9	21
−78	63.9	32.4	14

a) One equivalent of $Pb(OAc)_4$ was used in CH_2Cl_2 solution. b) Isolated yield. c) Determined by glc (PEG 20M, 180 °C).

Catalytic Effect: In general, a catalytic effect is regarded as another important factor which may govern a carbene reaction. It is well known that, in the presence of a catalyst, such as copper salt, some selectivity has been observed in carbene reactions.[22] We have tried copper(II) acetylacetonate ($Cu(acac)_2$) and cuprous chloride (CuCl) as catalysts. The former is soluble in organic solvents, and the latter, insoluble. The results were rather disappointing; they are summarized in Table 3. It can safely be said that a catalytic effect hardly works in these cases; under these conditions it is doubtful that the resulting carbene is actually modified by the copper ion.

TABLE 3. THE OXIDATION OF XI IN THE PRESENCE OF COPPER ION[a)]

Copper ion	Temp.	I/IV[b)]
$Cu(acac)_2$	Room temp.	11
$Cu(acac)_2$	−15 °C	16
CuCl	Room temp.	8

a) $Pb(OAc)_4$ in CH_2Cl_2 was added to the solution of XI and $Cu(acac)_2$ or CuCl in CH_2Cl_2. b) Determined by glc (PEG 20M, 180 °C).

The Effect of a Protic Solvent: It is well known that, in the presence of an appropriate proton source, a diazo compound is converted to a corresponding carbocation *via* a diazonium ion, the behavior of which is generally very different from that of a corresponding carbene.[11] Since the oxidation of XI by $Pb(OAc)_4$, NiPO, and active MnO_2 is accompanied by the production of acetic acid in the former case, and by that of water in the latter two cases, and since both acetic acid and water are able to become appropriate proton sources, we examined the selectivity of the oxidation reactions in the presence of a larger amount of the proton source. The results are summarized in Table 4. In the cases of NiPO and MnO_2 the addition of methanol diminished the ratio of I to IV; this implies that the selectivity is reduced in the carbocation process. In the case of $Pb(OAc)_4$ the addition of methanol or acetic acid did not cause any marked change in the ratio of I to IV; the reason for this is not clear, but if a carbene formation and a diazonium ion formation would compete each other, in the case of $Pb(OAc)_4$ I and IV would be produced predominantly *via* a carbene, and therefore the ratio of I to IV would not be affected.

TABLE 4. THE OXIDATION OF XI IN THE PRESENCE OF PROTON SOURCE

Run	Oxidant	H^+-Source	Additive	I/IV[a)]
1	$Pb(OAc)_4$	—	K_2CO_3	10.4
2	$Pb(OAc)_4$	AcOH	—	11.6
3	$Pb(OAc)_4$	MeOH	—	9.9
4	NiPO	—	$MgSO_4$	9.5
5	NiPO	MeOH	$MgSO_4$	5.9
6	MnO_2	—	$MgSO_4$	9.5
7	MnO_2	MeOH	$MgSO_4$	4.9

a) Determined by glc (PEG 20M, 180 °C).

Bamford-Stevens Reactions of II in Aprotic and Protic Solvents: In order to compare the results of the oxidation of XI, we effected the Bamford-Stevens reactions of II in aprotic as well as in protic solvents. It has been established that, in an aprotic solvent such as diglyme, the reaction proceeds *via* a carbene, whereas in a protic solvent such as ethylene glycol the reaction proceeds *via* a carbocation (diazonium ion).[11] The results obtained here are summarized in Table 5. In diglyme, more than 2.7 times as much of the IV olefin was produced as of the I cyclopropane, whereas in ethylene glycol more than 1.9—2.5 times as much of I was produced as of IV. It is of interest that the ratio of I to IV under aprotic conditions is inverted in comparison with that under protic conditions. These results are very informative in elucidating the cause of the selectivity.

Table 5. Bamford-Stevens reaction of II

$$\text{II} \xrightarrow[\text{Base, Solvent}]{140\ ^\circ\text{C}} \text{I} + \text{IV}$$

Solvent	Base (equiv.)	I : IV[a]
Diglyme	NaOMe (3.4)	1 : 2.7
Diglyme	NaH (1.9)	1 : 2.8
Ethylene glycol	Na (1.7)	1.9 : 1
Ethylene glycol	Na (3.4)	2.3 : 1
Ethylene glycol	Na (10)	2.5 : 1

a) Determined by glc (PEG 20M, 180 °C).

Mechanistic Considerations: As has been mentioned above, for an intramolecular carbene insertion reaction the distribution of the products seems to depend on the conformation of the corresponding carbene intermediate. In other words, the choice of the formation of cyclopropane and/or olefin is thought to depend on the degree of overlap of the γ-C–H bond and the β-C–H bond with the vacant sp^2-orbital of (singlet) carbene.

As to the conformation of the homoadamantane system, Schleyer *et al.* have argued on the basis of the obtained results in their studies of the infrared intramolecular hydrogen-bonding-shift of *cis*-4,5-homoadamantanediol and quantitative conformational analysis calculations.[23] According to them, the preferred conformation in the XIV homoadamantane system is essentially untwisted, but this system is so flexible that the dihedral angle varies from 0 to *ca.* 30° (see XIVa and XIVb in Fig. 1). In the XII carbene, the XIIa conformer might be very favorable for γ-C–H insertion producing I, while the XIIb conformer might be very favorable for producing IV. A model investigation[24] tells us that the 2-C–H$_a$ or 9-C–H$_a$ (γ-C–H) bond occupies a more favorable position to overlap with the sp^2-vacant orbital at C-4 (note that the 2-C–H$_a$ or 9-C–H$_a$ bond and the sp^2-vacant orbital at C-4 are coplanar) than 5-C–H$_b$ (β-C–H), while the dihedral angle between the 5-C–H$_b$ (β-C–H) bond and the sp^2-vacant orbital at C-4 is about 30°. For XIIb, the dihedral angle is about 0°, while the 2-C–H$_a$ or 9-C–H$_a$ bond and the sp^2-vacant orbital at C-4 are out-of-plane. At lower temperatures (oxidation conditions), the contribution of the XIIa conformer might be larger than that of XIIb because there is no strain due to the eclipsed form of C-4-H and C-5-H for XIIa, but XIIb might have some torsional strain. At higher temperatures (Bamford-Stevens conditions), the energy difference between XIIa and XIIb might be overcome by the temperature factor and the entropy factor might play an important role, so that the contribution of XIIb might be larger than that of XIIa.

In the VIII carbocation, at lower temperatures the contribution of the VIIIa conformer might be larger than that of VIIIb for the same reasons as in the case of XII. The reduced ratio of I to IV in the carbocation process is caused by the lower γ-C–H insertion ability of VIII than that of XII. At higher temperatures, however, VIIIa might also be more stable than VIIIb, since the VIIIb conformer might have some strain due to the eclipsed form of C-4-H and C-5-H.

We think that the selectivity in the oxidation of XI and the Bamford-Stevens reaction can be well explained by considering the conformations of the XII carbene and the VIII carbocation.

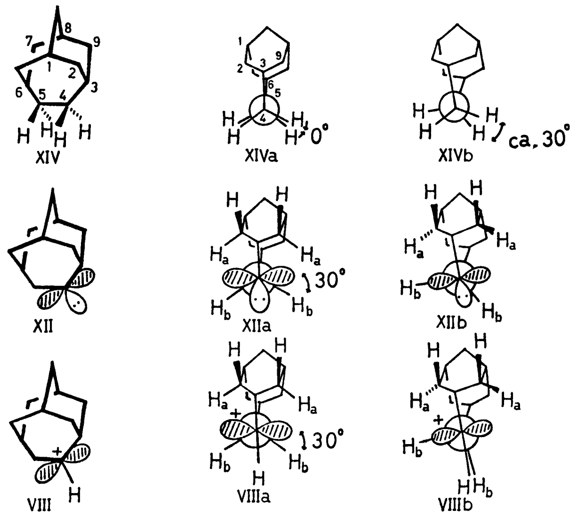


Fig. 1. Conformations of XIV, XII, and VIII.

In conclusion, lowering the reaction temperature in the intramolecular insertion reaction of XII promotes the γ-C–H insertion, thus producing I at the expense of the β-C–H insertion. At −78 °C, the oxidation of XI by Pb(OAc)$_4$ gives I exclusively. To date, this is the most efficient method of obtaining I.

Experimental

All the temperatures are uncorrected. The IR spectra were obtained on a Shimazu IR-27 spectrometer. The MS spectra were taken by using a Hitachi RMS-4 mass spectrometer. The PMR spectra were obtained on an EM-360 spectrometer, TMS being chosen as the internal standard.

Photochemical Synthesis of I. A mixture of IV (500 mg; 3.4 mmol) in 50 ml of xylene (a commercial mixture) containing methanesulfonic acid (0.5 ml) was irradiated by means of a 300 W medium-pressure mercury lamp under nitrogen for 7 day. The glc analysis (PEG 20 M, 180 °C) showed a 2: 1 mixture of I and IV. The reaction mixture was poured into water and neutralized by sodium hydrogen carbonate, and then the organic layer was collected and dried (Na$_2$SO$_4$). After the xylene solution has been passed through an alumina column to remove the acid throughly, the xylene was quickly removed under reduced pressure. The residue was chromatographed on a silver nitrate–alumina (15% silver nitrate) column. Elution by petroleum ether (40—50 °C) gave pure I (200 mg, 40%), while elution by petroleum ether-ether (8: 2) gave IV (90 mg). Compound I has the following properties: mp 226—229 °C (sealed tube) (lit,[5] mp 209—210 °C); MS: *m/e* 148 (M$^+$, 100%); PMR δ(CCl$_4$) 0.53—2.33 (broad complex multiplet); ^{13}C-NMR δ(CDCl$_3$, downfield from TMS, proton-decoupled) 38.80 (CH$_2$), 32.42 (2CH$_2$), 28.61 (2CH$_2$), 26.79 (2CH), 21.59 (CH), 12.78 (CH), 10.26 (2CH), measured by JEOL PS 100/PFT 100 (25.1 MHz).

Oxidation of XI by Pb(OAc)$_4$. A mixture of X (4.0 g; 24.4 mmol), 100% hydrazine hydrate (4.9 g; 97.6 mmol), and glacial acetic acid (1.7 g; 24.4 mmol) in 80 ml of anhydrous ethanol was refluxed for 4 hr under nitrogen. The reaction mixture was then cooled to room temperature, and the ethanol was removed under reduced pressure. Methylene chloride (CH_2Cl_2, 100 ml) was added to the residue, and the aqueous layer was separated. The organic layer was washed succesively with a 10% NaOH solution saturated with NaCl and with brine, and then dried ($CaCl_2$). Glc analysis showed that the CH_2Cl_2 solution contained XI (*ca.* 75%; mp 32—34 °C; MS: *m/e* 178 (M^+, 100%), 134 (72%). 93 (69%), 79 (49%); IR (Nujol) 3200, 2840, 1620, 1440, 1345, 1080 cm^{-1}; NMR $\delta(CCl_4)$ 1.15—1.04 (m, 16H), 4.50 (broad s, 2H, NH_2)) and V (*ca.* 25%; mp>290 °C; MS: *m/e* 149 (100%), IR (nujol) 2850, 1615, 1445, 1375, 1085, 940 cm^{-1}; NMR $\delta(CDCl_3)$ 1.25—3.21 (m)).[5] The $CaCl_2$ was filtered off, and $Pb(OAc)_4$ (12 g) free from AcOH in CH_2Cl_2 (120 ml) was added drop by drop to the above filtrate at -78 °C. The reaction mixture was stirred for 1.5 hr at -78 °C and then warmed to room temperature. After 40 ml of water has been added to the reaction mixture to quench the unreacted $Pb(OAc)_4$, the mixture was stirred overnight, filtered, washed succesively with a saturated $NaHCO_3$ solution and with brine, and dried ($CaCl_2$). After the removal of the CH_2Cl_2, the residue was chromatographed on alumina. Elution by *n*-hexane gave 2.29 g of hydrocarbon, which was shown by glc analysis to contain I (2.22 g, 61.5%) and IV (0.07 g, 1.9%). Elution by *n*-hexane–CH_2Cl_2 (1: 1) gave the VI acetate (0.69 g, 13.6%).

When other oxidants were employed, the procedures were essentially the same as that in the case of $Pb(OAc)_4$ except that the hydrazone solution was added to the CH_2Cl_2 solution containing the dispersed oxidant.

The azine (V) was recovered in the cases of NiPO and MnO_2, but not in the case of $Pb(OAc)_4$.

The Oxidation of XI in the Presence of a Protic Solvent. The procedures were essentially the same as that described above. The ratios of I to IV were determined by glc (PEG 20 M, 180 °C) (Table 4). In Run 1, K_2CO_3 was added as a neutralizing agent, but VI was still produced. In Run 2, $Pb(OAc)_4$ in CH_2Cl_2 was added to the solution of XI in CH_2Cl_2–AcOH (1: 1); a larger amount of VI was produced than in Run 1. In Run 3, $Pb(OAc)_4$ in CH_2Cl_2 was added to the solution of XI in CH_2Cl_2–MeOH (1: 1), and VI and 4-methoxyhomoadamantane (XIV) (MS: *m/e* 180 (M^+); NMR $\delta(CCl_4)$ 1.95—2.40 (broad m, 16H), 3.20 (s, 3H, OCH_3), 3.20—3.43 (m, 1H, $CHOCH_3$)[25] were produced. In Runs 4 and 6, $MgSO_4$ was added as a dehydrating agent, but XIII as well as X were produced in both cases. In Runs 5 and 7, the solution of XI in CH_2Cl_2 was added to a solution of CH_2Cl_2–MeOH (1: 1) containing an oxidant (NiPO or MnO_2) and $MgSO_4$; in both cases XIII, XIV, and X were produced.

Bamford-Stevens Reactions in Aprotic and Protic Solvents. 4-Homoadamantyl tosylhydrazone (II) was obtained by the standard procedure.[5,26] A mixture of II (332 mg, 1.0 mmol) and the base (NaOMe, 185 mg, 3.4 mmol; NaH, 100 mg, 1.9 mmol) in diglyme (5 ml, distilled over NaH) was heated at 140 °C for 1 hr. The reaction mixture was then cooled to room temperature and poured into water. The organic material were extracted with petroleum ether, washed with brine, and dried (Na_2SO_4). The solvent was then evaporated, and the residue was chromatographed on alumina. Elution by *n*-hexane gave the mixture of two hydrocarbons, I and IV (67.2 mg, 45%; 90.8 mg, 61%), the ratio of which was determined by glc. Elution by CH_2Cl_2 gave a small amount of V and an unidentified material.

Three kinds of mixtures of II (232 mg, 1.0 mmol) and Na (39 mg, 1.7 mmol; 78 mg, 3.4 mmol; 232 mg, 10 mmol) in 5 ml of ethylene glycol (distilled over Na) were heated at 140 °C for 1 hr. Each reaction mixture was cooled to room temperature and poured into water. The organic materials were extracted with petroleum ether, washed with brine, and dried (Na_2SO_4). The solvent was evaporated, and the residue was chromatographed on alumina. Elution by *n*-hexane gave two hydrocarbons, I and IV (53 mg, 36%; 34 mg, 23%; and 72 mg, 49%, respectively), the ratio of which was determined by glc. Elution by CH_2Cl_2 gave a trace amount of another material, which was presumably β-hydroxyethyl-4-homoadamantyl ether (XV) (MS: *m/e* 210 (M^+), 148 (100%); IR (neat) 3350, 2900, 1450, 1080 cm^{-1}; NMR δ, (CCl_4) 1.10—2.60 (broad m, 17H), 3.31—3.69 (broad m, 5H)), but its exact structure was not investigated further because the specimen was too small.

It was confirmed that I and VI were stable under the reaction conditions (excess base and excess sodium salt of *p*-toluenesulfinic acid in diglyme or ethylene glycol at 140 °C for 1 hr) of the control experiments.

References and Footnotes

1) Trivial nomenclature based on homoadamatane numbering; see reference 5.

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21) With NiPO and MnO_2, it was concluded that the lowest limit of the temperature at which the oxidation took place was 0—5 °C by observation of nitrogen evolved, but the yield was reduced and the ratio of I to IV was almost the same as that in the case of room temperature.

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