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REACTION OF 1-ADAMANTYL CATION WITH CARBON MONOXIDE IN THE PRESENCE OF ADAMANTANE AND TRIFLUOROMETHANESULFONIC ACID: A CONVENIENT ROUTE TO 3,4-HOMOADAMANTANEDIOL

KEN'ICHI TAKEUCHI, FUMIO AKIYAMA, TADAKAZU MIYAZAKI,
ITSUKO KITAGAWA, and KUNIO OKAMOTO*

Department of Hydrocarbon Chemistry, Faculty of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606, Japan

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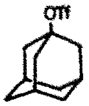
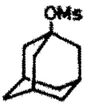
Abstract - The carbonylation of the 1-adamantyl cation with carbon monoxide in carbon tetrachloride at atmospheric pressure in the presence of trifluoromethanesulfonic acid (triflic acid) and adamantane affords 3-hydroxy-4-homoadamantyl 1-adamantanecarboxylate (2) in 70% yield under appropriate conditions. Among various 1-adamantyl cation precursors tested, 1-adamantyl trifluoromethanesulfonate (triflate) and methanesulfonate (mesylate) have given the best, comparable results. As to the acid catalyst, fluorosulfonic acid is less effective than triflic acid, and 100% sulfuric acid and methanesulfonic acid are completely ineffective to produce 2. It is recommended to use five mol each of triflic acid and adamantane per mol of 1-adamantyl mesylate or triflate. This reaction proceeds via the addition of the 1-adamantanecarbonyl cation to 1-adamantanecarbaldehyde, a transient intermediate, followed by the Wagner-Meerwein rearrangement. The hydroxy ester 2 is easily converted into 3,4-homoadamantanediol which is a promising starting material for 3,4-bifunctional homoadamantane derivatives.

The carbonylation of carbocations with carbon monoxide under strongly acidic conditions is well known as the Koch (or the Koch-Haaf) reaction.[1] The major products of this reaction are usually carboxylic acids. However, depending on the structure of a carbocation or by modifying reaction conditions, one can occasionally obtain ketones as major products.[2] A paper describes formation of esters (RCO_2R; R = cyclohexyl or 1-methyl-1-cyclopentyl) when cyclohexane is treated with carbon monoxide in the presence of a strong acid.[3] These esters, however, do not appear synthetically useful because of their low yields and little structural characteristics.

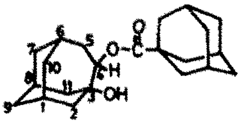
While we were exploring a new use of highly reactive 1-adamantyl trifluoromethanesulfonate (triflate) (AdOTf, **1a**),[4] we found that the reaction of AdOTf with carbon monoxide at atmospheric pressure in the presence of adamantane and trifluoromethanesulfonic acid (triflic acid, TfOH) affords 3-hydroxy-4-homoadamantyl 1-adamantanecarboxylate (2) in about 70% yield.[5] The ester 2 was easily converted into 3,4-homoadamantanediol (3) by saponification, which had never been synthesized by the other methods.



1a



1b



2

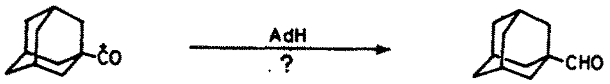
3

This reaction was thought to be unique because the 3,4-homoadamantanediol monoester (2) was obtained in a good yield under the conditions of the Koch reaction and because 2 and 3 are potentially useful starting materials toward 3,4-disubstituted homoadamantane derivatives. Consequently, we investigated the reaction conditions to increase the yield of 2 and the probable pathway to products. This paper describes the full account of the previous communication[5] and the use of 1-adamantyl methanesulfonate (mesylate) (AdOMs, **1b**) which is prepared much more conveniently and at a lower cost than AdOTf. It was found that 1-adamantyl mesylate can be used in the place of 1-adamantyl triflate (**1a**) without appreciable change in reaction conditions and product yields. 1-Bromoadamantane and 1-adamantanol were also tested, but the former gave 2 in a low yield and the latter yielded 1-adamantanecarboxylic acid as the sole product.

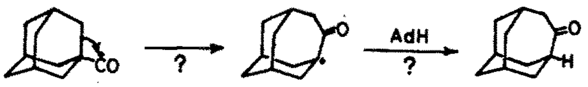
RESULTS AND DISCUSSION

Reaction of 1-Adamantyl Triflate with CO in the Presence of Triflic Acid. 1-Adamantyl triflate (**1a**) is unreactive toward carbon monoxide in carbon tetrachloride at atmospheric pressure at 0 - 30°C. However, on addition of triflic acid (five molar equivalent) at 0°C, rapid CO uptake was observed. After the CO uptake had stopped, the solution was quenched with cold water to give 1-adamantanecarboxylic acid (62%) and 1-adamantanol (35%). No ring-expansion product was detected.

Reaction of 1-Adamantyl Triflate with CO in the Presence of Adamantane and Triflic Acid. Initially we intended to convert the 1-adamantanecarbonyl cation, which is generated from the 1-adamantyl cation and CO, into 1-adamantanecarbaldehyde via hydride transfer from adamantane (AdH) (eq 1) or into 4-homoadamantanone via a rearrangement of the acyl cation followed by hydride transfer from adamantane (eq 2). However, those products were not detected by GLC and ^{1}H NMR.

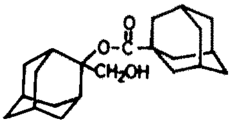


(1)



(2)

Close examination of the neutral products from the reaction conducted with 0.16 M AdOTf in CCl_4 (15 ml) and molar ratio AdOTf : TfOH : AdH = 1 : 3 : 1 under carbon monoxide of atmospheric pressure at 30°C for 20 h showed the formation of 2 (15%) and 2-hydroxymethyl-2-adamantyl 1-adamantanecarboxylate (**4**) (2.1%) (Table 1, entry 1). These products were easily separated from each other by column chromatography over silica gel. (Throughout this paper the product yields are based on the 1-adamantyl cation precursor.)



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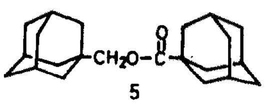

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Table 1. Product Yields in the Acid Catalyzed Reaction of Various 1-Adamantyl Cation Precursors with Carbon Monoxide and Adamantane (AdH) in CCl_4 at 30±2°C[a]

entry	AdX	acid	time	molar ratio (AdX=1)			product yield/%[c]					
			/h	acid	AdH	CO[b]	2	4	5	$AdCO_2H$	AdOH	total
1	AdOTf	TfOH	20	3	1	1.2	15	2.1	0	40	0	57
2	AdOTf	TfOH	20	3	5	1.9	37	4.3	13	40	0	94
3	AdOTf	TfOH	20	5	5	2.7	70	6.9	21	39	0	137
4	AdOTf	TfOH	20	10	5	3.0	72	8.0	19	103	0	202
5	AdOMs	TfOH	0.2	5	5	2.0	47	3.3	14	63	0	127
6	AdOMs	TfOH	3	5	5	2.8	61	4.3	19	50	0	134
7	AdOMs	TfOH	20	5	5	2.5	71	4.3	18	42	0	135
8[d]	AdOMs	TfOH	20	5	5	2.7	67	5.8	24	58	0	155
9[e]	AdOMs	TfOH	20	5	5	2.1	60	4.1	6.7	58	0	129
10[f]	AdOMs	TfOH	20	5	5	2.0	53	1.5	25	70	17	167
11	AdOMs	FSO_3H	20	5	5	2.9	39	2.3	4.5	199	4.6	249
12	AdOMs	H_2SO_4	20	5	5	1.7	0	0	0	172	0	172
13	AdOMs	MsOH	20	5	5	0.6	0	0	0	65	11	76
14	AdBr	TfOH	20	5	5	2.5	30	4.4	32	70	0	136
15	AdOH	TfOH	20	5	5	1.1	0	0	0	106	0	106

a) A solution (8.0 or 15 ml) of 0.14 or 0.16 M AdX in CCl_4 was used except for entries 8 and 9. b) CO consumed. c) 100 x (product, mol)/(AdX, mol); isolated yield. d) A solution (50 ml) of 0.23 M AdOMs in CCl_4 was used. e) A solution (16 ml) of 0.071 M AdOMs in CCl_4 was used. f) At 0°C.

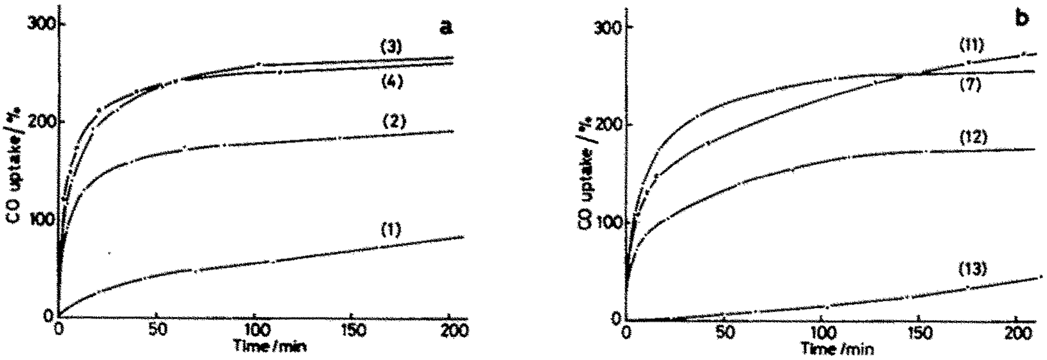


Fig. 1. Plots of CO uptake (mol% on **1a** or **1b**) against reaction time for the reaction of 1-adamantyl triflate (**1a**) (Fig. 1a) and 1-adamantyl mesylate (**1b**) (Fig. 1b). The number in parentheses denotes the entry in Table 1.

When the amount of adamantane was increased to five molar equivalent (Table 1, entry 2), the CO uptake was accelerated (Fig. 1a) and the yields of **2** and **4** increased to 37 and 4.3%, respectively. Besides, the third ester, (1-adamantyl)methyl 1-adamantanecarboxylate (**5**) (13%) was obtained. With the molar ratio, AdOTf : TfOH : AdH = 1 : 5 : 5, the esters **2**, **4**, and **5** were obtained in 70, 6.9, and 21%, respectively (Table 1, entry 3). An increase in the amount of TfOH to 10 molar equivalent merely increased the yield of 1-adamantanecarboxylic acid, leaving the rate of CO uptake and the yield of **2** essentially unchanged (Fig. 1a; Table 1, entry 4). These results suggest that an appropriate molar ratio among AdOTf, TfOH, and AdH to attain a good yield of **2** would be 1 : 5 : 5.

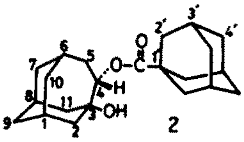
In the absence of 1-adamantyl triflate, with the other conditions being the same with those of entry 3, **2** was obtained only in 0.8% yield based on adamantane. Although the 1-adamantyl cation is slowly generated from adamantane in triflic acid by protolysis,[6] the presence of an easily ionizing 1-adamantyl derivative is essential to prepare **2** in a good yield.

The structure of the new compounds (2 and 4) was determined on the basis of IR, ^{1}H NMR, and ^{13}C NMR spectra. All the data are summarized in Table 2. The known ester 5[7] was identified from the melting point and by comparing the spectral data with those of an authentic sample.

Table 2. IR, ^{1}H NMR (60 MHz), and ^{13}C NMR (25 MHz) Data of 2 and 4.[a]

compound	2		4	
IR(CCl_4) /cm^{-1}	3600, 3470(br) 1725, 1230, 1075		3610, 3490(br) 1728, 1230, 1075	
^{1}H NMR (CCl_4) δ/ppm	4.72(dd, 1H, J 10.4, 3.4 Hz, H-4) 2.3(s, 1H, -OH) 1.3-2.2(br. m, 30H)		4.15(s, 2H, H-11) 1.3-2.5(br. m, 30H)	
^{13}C NMR[b] δ/ppm	177.2(s, CO) 73.5(s,C-3) 40.7(s,C-1') 39.2(t,C-2)[c] 36.9(t,C-7)[c] 36.4(t,C-4') 29.8(d,C-6)[d] 27.6(d,C-8)[d]	80.5(d,C-4) 42.6(t,C-5)[c] 40.0(t,C-11)[c] 38.8(t,C-2') 36.8(t,C-10)[c] 35.5(t,C-9)[c] 27.8(d,C-3') 27.4(d,C-1)[d]	177.1(s, CO) 68.4(t,C-11) 38.6(t,C-2') 36.1(t,C-4') 34.0(t,C-10)[g,h] 27.8(d,C-3') 27.0(d,C-5)[i]	73.8(s,C-2) 40.7(s,C-1') 37.8(t,C-6) 34.5(d,C-3)[e] 32.2(t,C-4)[f,h] 27.4(d,C-7)[i]

a) The numbering systems are as follows:



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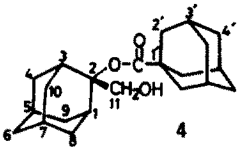

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b) 2 in $CDCl_3$ and 4 in CD_2Cl_2. c) The signals for C-2, C-5, C-7, C-9, C-10, and C-11 may be interchangeable. d) The signals for C-1, C-6, and C-8 may be interchangeable. e) C-3 is equivalent to C-1. f) C-4 is equivalent to C-9. g) C-10 is equivalent to C-8. h) The signals for C-4 (or C-9) and C-10 (or C-8) may be interchangeable. i) The signals for C-5 and C-7 may be interchangeable.

Reaction of 1-Adamantyl Mesylate, Bromide, or Alcohol with CO in the Presence of Adamantane and Triflic Acid. 1-Adamantyl mesylate (1b) can be prepared from 1-adamantanol and methanesulfonyl chloride in a good yield.[8] It is much more stable to moisture than the triflate, permitting convenient handling. With 1.14 mmol of AdOMs in 8.0 ml CCl_4 ([AdOMs] = 0.14 M) and the molar ratio, AdOMs : TfOH : AdH = 1 : 5 : 5, at 30°C for 20 h, the esters 2, 4, and 5 were obtained in 71, 4.3, and 18%, respectively (Table 1, entry 7). A larger scale reaction by using 11.4 mmol of AdOMs in 50 ml CCl_4 ([AdOMs] = 0.23 M) was easily carried out without appreciable change in the yield of 2 (Table 1, entry 8). Thus, it is no longer necessary to use 1-adamantyl triflate as a cation source. A lower temperature (0°C; Table 1, entry 10) and decreased reaction time (0.2 and 3 h; Table 1, entries 5 and 6) were unfavorable to increase the yield of 2.

It is noteworthy that the yield of 5 decreases as the concentrations of AdOMs, TfOH, and adamantane are decreased. As entry 9 of Table 1 shows, when their concentrations were reduced to half as compared with entry 7, the yield of 5 decreased to 6.7%. In contrast, when their concentrations were increased by 1.6 times, it increased to 24% (Table 1, entry 8). Perhaps, the yield of 5 is most affected by the concentration of adamantane. This is supported by the fact that 5 was not detected when the reaction of AdOTf was conducted with an equivalent amount of adamantane instead of five equivalent (Table 1, compare entries 1 and 2). Mechanistic significance for the formation of 5 will be discussed in the following section.

It is well known that alkyl mesylates are much less reactive than alkyl triflates in ionizing solvents. For example, alkyl mesylates solvolyze 10^5 - 10^6 times slower than the corresponding triflates under S_N1 conditions.[9] Nevertheless, both AdOTf and AdOMs reacted at a comparable rate in the present carbonylation reaction as demonstrated by their similar rates of CO uptake (Fig. 1). Therefore, the rate-controlling step of the present reaction is not the ionization step of AdOTf or AdOMs, but most probably the step of hydride transfer from adamantane to the 1-adamantanecarbonyl cation to form 1-adamantanecarbaldehyde as a transient key intermediate. The intermediacy of the aldehyde will be shown in a later section.

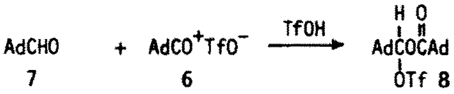
With a view to finding out a more economical method, fluorosulfonic acid, 100% sulfuric acid, and methanesulfonic acid were examined. However, the use of fluorosulfonic acid resulted in much slower CO uptake and a lower yield of 2 (39%) than when TfOH was used (Fig. 1b; Table 1, entry 11). Sulfuric and methanesulfonic acids were completely ineffective for the preparation of 2 (Fig. 1b; Table 1, entries 12 and 13).

Attempts to use 1-bromoadamantane or 1-adamantanol in the place of AdOTf and AdOMs were made, but the former gave 2 in a poor yield (30%) and the latter only 1-adamantanecarboxylic acid (Table 1, entries 14 and 15).

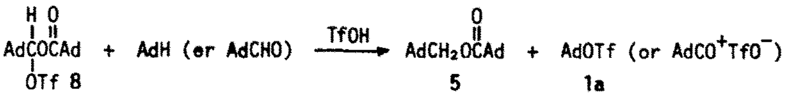
Probable Pathways to the Esters 2, 4, and 5. The formation of the three esters (2, 4, and 5) can reasonably be explained by postulating transient formation of 1-adamantanecarbaldehyde (**7**) as a key intermediate. The formation of the 1-adamantanecarbonyl cation (**6**) from AdOTf or AdOMs and CO (eq 3) is the first step of the Koch reaction. The acyl cation (**6**) abstracts hydride from adamantane to give 1-adamantanecarbaldehyde (**7**) in the presence of triflic acid (eq 4). Nucleophilic attack of 7 to 6 gives a triflate 8 (eq 5), which gives 5 on hydride abstraction from adamantane (or 7)(eq 6). The Wagner-Meerwein rearrangement of 8 gives a triflate 2-Tf (eq 7). Subsequent intramolecular hydride shift in 2-Tf followed by the Wagner-Meerwein rearrangement would afford 4-Tf (eq 7). When the mixture is worked up with water, 2-Tf and 4-Tf should afford 2 and 4, respectively. Summing up eqs 3 - 7, one can describe the stoichiometries for the formation of the esters 2-Tf, 4-Tf, and 5 by eq 8, 9, and 10, respectively. The results that the total product yields exceed 100% on the basis of AdOTf or AdOMs (Table 1) should be due to slow formation of the 1-adamantyl cation from adamantane by protolysis.

$$\underset{\mathbf{1a}}{\mathrm{AdOTf}} + \mathrm{CO} \xrightarrow{\mathrm{TfOH}} \underset{\mathbf{6}}{\mathrm{AdCO^+TfO^-}} \qquad (3)$$

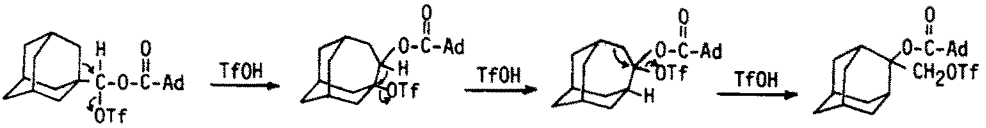
$$\underset{\mathbf{6}}{\mathrm{AdCO^+TfO^-}} + \mathrm{AdH} \xrightarrow{\mathrm{TfOH}} \underset{\mathbf{7}}{\mathrm{AdCHO}} + \underset{\mathbf{1}}{\mathrm{AdOTf}} \qquad (4)$$



$$\underset{\mathbf{7}}{\mathrm{AdCHO}} + \underset{\mathbf{6}}{\mathrm{AdCO^+TfO^-}} \xrightarrow{\mathrm{TfOH}} \mathrm{Ad}\overset{\mathrm{H}}{\underset{\mathrm{OTf}}{\mathrm{C}}}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ad}\ \mathbf{8} \qquad (5)$$



$$\mathrm{Ad}\overset{\mathrm{H}}{\underset{\mathrm{OTf}}{\mathrm{C}}}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ad}\ \mathbf{8} + \mathrm{AdH\ (or\ AdCHO)} \xrightarrow{\mathrm{TfOH}} \underset{\mathbf{5}}{\mathrm{AdCH_2O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ad}} + \underset{\mathbf{1a}}{\mathrm{AdOTf}}\ (\mathrm{or\ AdCO^+TfO^-}) \qquad (6)$$



3 2-Tf 4-Tf (7)

Ad = 1-adamantyl

$$\mathrm{AdOTf} + \mathrm{AdH} + 2\,\mathrm{CO} \longrightarrow \textbf{2}\text{-Tf} \qquad (8)$$

$$\mathrm{AdOTf} + \mathrm{AdH} + 2\,\mathrm{CO} \longrightarrow \textbf{4}\text{-Tf} \qquad (9)$$

$$2\,\mathrm{AdH} + 2\,\mathrm{CO} \longrightarrow \textbf{5} \qquad (10)$$

Reactions similar to those described in eqs 3 - 6 are found in the literature. The equilibrium of 1-adamantyl cation and carbon monoxide with 1-adamantanecarbonyl cation (eq 3) has been quantitatively studied in FSO_3H-SbF_5.[10,11] Abstraction of methine hydride by an acyl cation (eq 4) may be thermodynamically unfavorable. However, that this kind of process could occur has been postulated between the acetyl cation and isobutane in HF-BF_3[12] and explained by postulating a highly reactive, protonated acyl cation.[13] A patent describes the formation of 1-adamantanecarbaldehyde (**7**) from adamantane and carbon monoxide in the presence of aluminum chloride.[14] The addition of the acyl cation **6** to **7** (eq 5) is analogous to the reaction of an acyl chloride (R'COCl) with an aldehyde (RCHO) to form 1-chloroalkyl carboxylate (RCHClOCOR') in the presence of zinc chloride.[15] Ring-expansion similar to that of **8** to **2**-Tf (eq 7) has often been reported for various reactions of (1-adamantyl)methyl derivatives.[16,17]

The step of the formation of the ester **5** (eq 6) is mechanistically different from a related reaction described in the literatre.[12] Brouwer and Kiffen found that ethyl acetate was formed in the reaction of the acetyl cation and isobutane in HF-BF_3.[12] This was explained by assuming two-step hydride transfer from isobutane to the acetyl cation to give ethanol followed by acetylation of the ethanol.[12] If such is the case, the ester **5** might have been produced from (1-adamantyl)methanol and the acyl cation **6** (eqs 11 - 13). At present we are not in the position to determine which of the process be at work. No matter which process of eq 6 or eqs 11 - 13 be followed, the diminished concentration of adamantane will decrease the yield of **5**.

$$\underset{\textbf{7}}{\mathrm{AdCHO}} + \mathrm{H}^{+} \longrightarrow \mathrm{Ad}\overset{+}{\mathrm{C}}\mathrm{HOH} \qquad (11)$$

$$\mathrm{Ad}\overset{+}{\mathrm{C}}\mathrm{HOH} + \mathrm{AdH} \longrightarrow \mathrm{AdCH_2OH} + \mathrm{Ad}^{+} \qquad (12)$$

$$\mathrm{AdCH_2OH} + \underset{\textbf{6}}{\mathrm{Ad}\overset{+}{\mathrm{C}}\mathrm{O}} \longrightarrow \underset{\textbf{5}}{\mathrm{AdCH_2OCOAd}} + \mathrm{H}^{+} \qquad (13)$$

Evidence for the Formation of 1-Adamantanecarbaldehyde as an Intermediate. Although we were unable to detect 1-adamantanecarbaldehyde (**7**) even in early stages of the reaction, its possible existence was supported by confirming that **2** was formed in the reaction of AdOTf with carbon monoxide and the aldehyde **7** in the presence of triflic acid. The results are shown in Table 3. It is noted that **2** was formed in a yield as high as 94% (based on the aldehyde) (Table 3, entry 2).

Table 3. Product Yields in the Triflic Acid Catalyzed Reaction of 1-Adamantyl Triflate with Carbon Monoxide and 1-Adamantanecarbaldehyde (AdCHO) in CCl_4.[a]

entry	temp.	time	molar ratio (AdCHO=1)			product yield/%		
	/°C	/h	AdOTf	TfOH	CO[b]	**2**[c]	$AdCO_2H$[d]	others[d]
1	30	22	1	5	e	46	34	ca.24[f]
2	0	3	1.3	5	1.3	94	21	2[g]

a) A solution (9.4 ml) of 0.16 M AdOTf in CCl_4 was used. b) CO consumed. c) Based on AdCHO. d) Based on AdOTf. e) Not determined. f) Mainly 1-chloroadamantane. g) 1-Adamantanol.

When deuterated 7 (AdCDO, 98%-d) was used under the conditions of entry 2 of Table 3, the produced ester 2 was found by means of ^{13}C NMR to contain almost all (96%-d) the deuterium at the 4-position as predicted from the postulated pathway (eqs 3 - 7).

Synthesis of 3,4-Homoadamantanediol and 3-Hydroxy-4-homoadamantanone. Although 3,4-homoadamantanediol (3) is thought to be a promising starting material to 3,4-disubstituted homoadamantane derivatives, it has never been synthesized by the other methods. Saponification of the ester 2 in ethanolic KOH afforded the diol quantitatively. However, oxidation of the diol to 3-hydroxy-4-homoadamantanone with pyridinium chlorochromate[18] or Jones reagent[19] proceeded only in low yields (20 - 30%). The difficulty in selectively oxidizing a secondary OH adjacent to a tertiary OH has often been described in the literature.[20] The physical properties and spectral data of 3 and 3-hydroxy-4-homoadamantanone are given in the experimental section.

EXPERIMENTAL

M.p.s are uncorrected. Elemental analyses were performed by the Microanalytical Center, Kyoto University. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Hitachi R-24 (60 MHz) and a JEOL FX100 (25 MHz) instrument, respectively. IR spectra were measured with a Hitachi 215 spectrophotometer.

Materials. All reagents were of reagent-grade quality except when otherwise noted. 1-Adamantyl mesylate (1b) was prepared as described in the literature[8] and recrystallized from dry pentane; yield: 64%; m.p. 48.5 - 50.0°C (dec) [lit.[8] 46 - 48°C (dec)]. Authentic (1-adamantyl)-methyl 1-adamantanecarboxylate (5) was prepared from (1-adamantyl)methanol and 1-adamantanecarbonyl chloride in pyridine and recrystallized from hexane, m.p. 247.0 - 249.0°C (lit.[7] 247 - 250°C). 1-Adamantanecarbaldehyde (7) was prepared by the oxidation of (1-adamantyl)methanol with pyridinium chlorochromate in dichloromethane as described in the literature,[18] and the crude product (yellowish solid) was used immediately without purification; the purity estimated by ^{1}H NMR was ca. 95%. 100% Sulfuric acid was prepared by adding 25% fuming sulfuric acid (5.33 g) to 97% sulfuric acid (10.0 g). Pentane, hexane, dichloromethane, and carbon tetrachloride were refluxed over P_2O_5 and distilled.

1-Adamantyl triflate (1a) in Hexane. The method described previously[4] was slightly modified. All glassware was dried in an oven and stored in a desiccator over silica gel. In a 300 ml pear-shaped flask flushed with dry nitrogen were placed 1-bromoadamantane (12.0 g, 55.9 mmol), anhydrous hexane (150 ml), and 2,6-di-t-butyl-4-methylpyridine (1.5 g, 7.3 mmol) as a stabilizer, and the mixture was magnetically stirred in an ice-water bath until the bromide dissolved. To the stirred solution was added silver triflate (15.1 g, 65.2 mmol) in one portion and the suspension stirred at 0°C under nitrogen in the dark overnight. Most of the supernatant solution was transferred under nitrogen into another pear-shaped flask provided with a three-way stopcock by means of a syringe and stored in a refrigerator. The concentration of 1a was determined by pouring the solution (2.000 ml) into ethanol in a 20 ml measuring flask, diluting to 20.00 ml with ethanol, and titrating 2.000 ml aliquots in acetone (6 ml) for the liberated triflic acid with standardized KOH in ethanol by using bromcresol green - methyl red mixed indicator. The yield of 1a was nearly quantitative.

1-Adamantyl Triflate (1a) in Carbon Tetrachloride. From the hexane solution of 1a of a known volume was evaporated the hexane with a rotary evaporator at 5 - 10 mmHg, the evaporating flask being immersed in an ice-water bath during evaporation. The crystalline, white residue was dissolved in anhydrous carbon tetrachloride to form a 0.14 or 0.19 M solution and immediately used for carbonylation.

1-Adamantanecarbaldehyde-α-d_1 (AdCDO). 1-Adamantanecarboxylic acid (3.32 g, 18.4 mmol) was reduced with $LiAlD_4$ (98%-d) (0.772 g, 18.4 mmol) in boiling THF (51 ml) to give essentially pure (1-adamantyl)methanol-α,α-d_2 ($AdCD_2OH$), which was recrystallized from ligroin; yield: 91%; m.p. 116.5 - 117.5°C (lit.[21] 115°C for $AdCH_2OH$). The alcohol (2.77 g, 16.5 mmol) was oxidized with pyridinium chlorochromate (5.43 g, 25.2 mmol) in dichloromethane (59 ml) as described in the literature,[18] and the produced crude aldehyde (yellowish solid) was used immediately without purification.

Reaction of 1-Adamantyl Triflate (1a) with CO in the Presence of Adamantane and TfOH. The procedure for entry 3 of Table 1 is shown as a typical example. A 25 ml three-necked flask equipped with a thermometer and containing adamantane (1.58 g, 11.6 mmol) was connected to a CO gas buret through a three-way stopcock and a Molecular Sieves 5A tube. The flask was evacuated and filled with dry CO gas. A solution of 1-adamantyl triflate (2.33 mmol) in anhydrous carbon tetrachloride (15 ml) was introduced through a septum cap and the solution was magnetically stirred in a 30 ± 2°C bath to attain thermal equilibrium. On injection of triflic acid (1.0 ml, 11.3 mmol), rapid CO uptake was observed. After 20 h the amount of CO consumed was 6.2 mmol. The reaction mixture was cooled in an ice-water bath, quenched with ice-cold water (15 ml), extracted with ether (70 ml), and the ether extract was washed with 5% NaOH solution (3 x 20 ml) and then with 10% NaCl solution (40 ml). The neutral compounds from the ether layer were chromatographed over silica gel (40 g) by using hexane and hexane-ether as eluent to give adamantane (0.897 g, 6.59 mmol), 5 (0.163 g, 0.497 mmol; 21%), 4 (0.055 g, 0.16 mmol; 6.9%), and 2 (0.560 g, 1.62 mmol; 70%) in this sequence. The aqueous layer was acidified and extracted with ether to give 1-adamantanecarboxylic acid (0.163 g, 0.902 mmol). 2; m.p. 249°C (dec) (from hexane-benzene); Found: C, 76.62; H, 9.29. Calc for $C_{22}H_{32}O_3$: C, 76.71; H, 9.36%. 4; m.p. 256.5°C (dec) (from hexane-benzene); Found: C, 77.01; H, 9.55. Calc for $C_{22}H_{32}O_3$: C, 76.71; H, 9.36%. 5: m.p. 245.5 - 247.5°C (from hexane) (lit.[7] 247 - 250°C). The IR, ^{1}H NMR, and ^{13}C NMR spectra of 5 were identical with those of an authentic sample which was prepared from (1-adamantyl)methanol and 1-adamantanecarbonyl chloride. The spectral data of 2 and 4 are summarized in Table 2.

Reaction of 1-Adamantyl Mesylate (1b) with CO in the Presence of Adamantane and a Strong Acid. The procedure for entry 7 of Table 1 is shown as a typical example. A 25 ml three-necked flask containing 1-adamantyl mesylate (0.263 g, 1.14 mmol) and adamantane (0.776 g, 5.71 mmol) was connected to a CO gas buret through a three-way stopcock and a Molecular Sieves 5A tube. The flask was evacuated and filled with dry CO gas. Anhydrous carbon tetrachloride (8 ml) was introduced through a septum cap and the solution was magnetically stirred in a 30 ± 2°C bath to attain thermal equilibrium. On injection of triflic acid (0.51 ml, 5.7 mmol), rapid CO uptake was observed. After 20 h the amount of CO consumed was 2.9 mmol. The reaction mixture was cooled in an ice-water bath, quenched with ice-cold water (20 ml), extracted with ether, and the ether extract was washed with 10% NaOH solution and dried ($MgSO_4$). The neutral compounds from the ether layer were chromatographed over silica gel (35 g) by using hexane-ether as eluent to give adamantane (0.467 g, 3.43 mmol), 5 (0.067 g, 0.204 mmol; 18%), 4 (0.017 g, 0.049 mmol; 4.3%), and 2 (0.278 g, 0.807 mmol; 71%) in this sequence. The aqueous layer was acidified and extracted with ether to give 1-adamantanecarboxylic acid (0.087 g, 0.483 mmol; 42%).

Reaction of 1-Adamantyl Triflate (1a) with CO in the Presence of AdCHO (7) (or AdCDO) and TfOH. A 25 ml three-necked flask connected to a CO gas buret through a three-way stopcock and a Molecular Sieves 5A tube was evacuated and filled with dry CO gas. A solution of 0.19 M AdOTf in anhydrous carbon tetrachloride (8.0 ml) stabilized by 2,6-di-t-butyl-4-methylpyridine (0.02 M) and that of 0.80 M AdCHO in carbon tetrachloride (1.43 ml) were introduced through a septum cap and the solution was magnetically stirred in an ice-water bath to attain thermal equilibrium. On injection of triflic acid (0.51 ml, 5.71 mmol), rapid CO uptake was observed, which was complete in 20 min. After 3 h the reaction mixture was quenched with ice-cold water (20 ml), extracted with ether, and the extract was washed with 10% NaOH solution and dried ($MgSO_4$). The neutral products from the ether extract were chromatographed over silica gel (24 g) by using hexane-ether as eluent to give 2 (1.07 mmol) in a yield of 94% based on AdCHO.

Saponification of 2 to 3,4-Homoadamantanediol (3). A solution of 2 (2.22 g, 6.43 mmol) and KOH (2.45 g, 43.7 mmol) in ethanol (38 ml) was heated at reflux for 2 h. Most of the ethanol was evaporated and then the residual yellowish solid was dissolved in 50 ml water. The aqueous solution was extracted with ether (3 x 30 ml), and the combined extracts were washed with 10% NaCl solution (2 x 20 ml), and dried ($MgSO_4$). Evaporation of the ether afforded essentially pure 3 (1.16 g, 99%), which on recrystallization from hexane-benzene gave pure 3 in 86% yield; m.p. 299 -301°C; IR ($CHCl_3$) 3550 br, 3400 br, 2910 s, 1450 m, 1080 m, 1037 m, 985 w, 955 w, 925 w, 895 w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2 - 2.4 (br. m, 15 H), 3.1 (br., 2 H, -OH), 3.67 (dd, 1 H, J = 4.0, 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 27.4 (d), 27.9 (d), 29.5 (d), 35.2 (t), 35.8 (t), 38.4 (t), 38.7 (t), 40.5 (t), 44.3 (t), 74.2 (s), 77.9 (d). Found: C, 72.19; H, 10.03. Calc for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95%.

Oxidation of 3,4-Homoadamantanediol (3) to 3-Hydroxy-4-homoadamantanone with Pyridinium Chlorochromate. The procedure of Corey[18] was followed. To a suspension of pulverized pyridinium chlorochromate (0.79 g, 3.7 mmol) in 6 ml CH_2Cl_2 was added 3 (0.444 g, 2.44 mmol) in 4 ml CH_2Cl_2 in one portion and the mixture was magnetically stirred at ambient temperature for 1.5 h. Anhydrous ether (10 ml) was added and the solution was passed through a column of Florisil (3.5 g). The residue in the flask was washed with anhydrous ether (3 x 5 ml) and the combined ether solutions were also treated with the above Florisil column. Evaporation of the solvent gave a greenish semisolid (0.32 g), which was chromatographed over silica gel (8 g) by using hexane-ether (7:3) as eluent to give 4-oxo-3-homoadamantanol (0.135 g) in 30% yield; m.p. 242.5 - 244.5°C (from hexane); IR (CCl_4) 3470 m, 2905 s, 2842 m, 1683 s, 1440 m, 1396 m, 1250 m, 1100 s, 1063 s cm^{-1}; ^{1}H NMR (CCl_4) δ 1.3 - 2.0 (m, 9 H), 2.2 (br. s, 4 H), 2.6 (d, 2 H, J = 3.0), 4.0 (s, 1 H, -OH); ^{13}C NMR ($CDCl_3$) δ 26.1 (d), 28.2 (d), 34.1 (t), 36.2 (t), 40.6 (t), 46.4 (t), 77.5 (s), 215.0 (s). Found: C, 73.01; H, 9.08. Calc for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

Oxidation of 3,4-Homoadamantanediol (3) to 3-Hydroxy-4-homoadamantanone with Chromic Acid. The chromic acid solution was prepared as described by Eisenbraun.[19] To a solution of 3 (2.35 g, 12.9 mmol) in acetone (150 ml) was added the chromic acid solution (4.0 ml) over 3 h, while the temperature was kept below 26°C. The solution was decanted and to this was added 2-propanol (2 ml) to destroy the excess chromic acid. Sodium hydrogen carbonate (3.3 g) was added and the mixture vigorously stirred until neutral to pH paper. After filtration, the acetone was evaporated and the residue was dissolved in ether (50 ml). The ether solution was washed with 10% NaCl solution (30 ml) and dried ($MgSO_4$). The crude product was chromatographed over silica gel by MPLC by using hexane-ether (3 : 2) as eluent to give the acetone ketal of **3** (1.12 g, 5.04 mmol; 39%) and 3-hydroxy-4-homoadamantanone (0.418 g, 2.32 mmol; 18%) in this sequence. Acetone ketal of **3**: m.p. 50.0 - 51.0°C; IR (CCl_4) 2900 s, 1380 s, 1370 s, 1250 s, 1220 s, 1170 s, 1080 s, 1050 s cm^{-1}; ^1H NMR (CCl_4) δ 1.23 (s, 3 H), 1.37 (s, 3 H), 1.4 - 2.6 (br., 15 H), 3.85 (t, 1 H, $J = 8.6$ Hz); ^{13}C NMR ($CDCl_3$) δ 26.8 (q), 27.8 (d), 27.8 (d), 28.0 (t), 28.8 (q), 31.6 (t), 34.6 (t), 36.0 (t), 38.3 (t), 41.6 (t), 43.4 (t), 82.7 (s), 82.7 (d), 107.3 (s). Found: C, 75.33; H, 10.06. Calc for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97%.

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