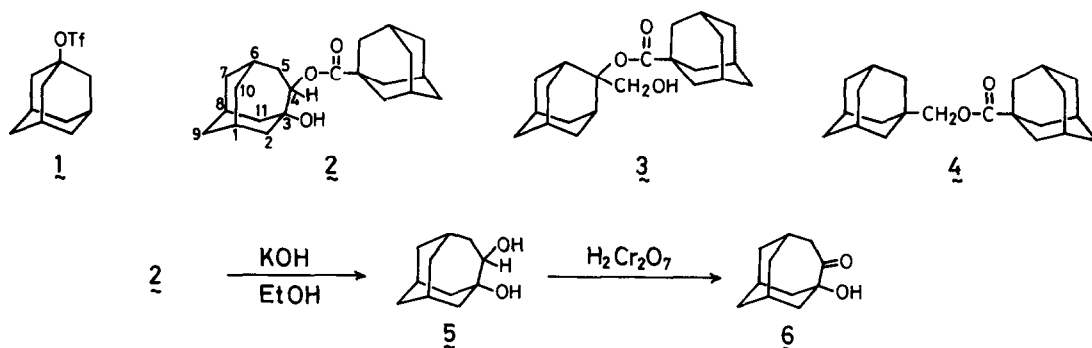


A FACILE SYNTHESIS OF 3,4-HOMOADAMANTANEDIOL VIA THE REACTION OF  
1-ADAMANTYL TRIFLATE WITH CARBON MONOXIDE

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**Abstract.** The reaction of 1-adamantyl triflate (1) with carbon monoxide and adamantane catalyzed by triflic acid affords 3-hydroxy-4-homoadamantyl 1-adamantanecarboxylate (2) as a major product, which is easily converted to 3,4-homoadamantanediol (5) — a promising starting material for 3,4-bifunctional homoadamantane derivatives.

Although various routes have been proposed for the preparation of the homoadamantane (tricyclo[4.3.1.1<sup>3,8</sup>]undecane) skeleton,<sup>1a</sup> the route via the one-step ring-expansion of 1-adamantyl cation has been limited to its reaction with acetylene to give 3-methylhomoadamantan-4-one via a vinyl cation.<sup>1b</sup> Previously, we described a facile synthesis and the high reactivity of 1-adamantyl triflate (1).<sup>2</sup> We now wish to report that 3-hydroxy-4-homoadamantyl 1-adamantanecarboxylate (2) is obtained as a major product in the reaction of 1 with carbon monoxide and adamantane in carbon tetrachloride at atmospheric pressure in the presence of triflic acid (trifluoromethanesulfonic acid, TfOH) as catalyst. Besides 2, two kinds of esters, 3 and 4, and 1-adamantanecarboxylic acid are obtained. Treatment of 2 with ethanolic KOH yields 3,4-homoadamantanediol (5), which is not easily accessible by the other methods.<sup>3</sup> Oxidation of 5 with chromic acid affords 3-hydroxy-4-homoadamantanone (6), which may be converted to various 3,4-bifunctional homoadamantane derivatives.<sup>4</sup>



The amount of CO uptake and the yields of the three kinds of esters depend on the mole ratio among 1, triflic acid, and adamantane (Table 1 and Fig. 1). Although the reaction conditions have not been optimized to attain a maximum yield of 2, the conditions of entry 3 (Table 1) appear appropriate. The following procedure is representative. A four-necked flask containing adamantane (46.5 mmol) was filled with dry carbon monoxide and connected to a CO gas

Table 1. Product Yields in the Triflic Acid Catalyzed Reaction of 1-Adamantyl Triflate (1) with Carbon Monoxide and Adamantane in Carbon Tetrachloride at  $30 \pm 2$  °C for 20 hr.<sup>a</sup>

entry	starting mole ratio				product yield <sup>d</sup> /%				
	1	TfOH	AdH <sup>b</sup>	CO <sup>c</sup>	2	3	4	1-AdCO <sub>2</sub> H	Total
1	1	3	1	1.2	15	2.1	— <sup>e</sup>	40	57
2	1	3	5	1.9	37	4.3	13	40	94
3	1	5	5	2.7	70	6.9	21	39	137
4	1	10	5	3.0	72	8.0	19	103	202

a) Generally, 15 ml of the 0.16 M solution of 1 stabilized by 2,6-di-*t*-butyl-4-methylpyridine (0.03 M) was used. b) Adamantane. c) CO consumed. d) [(moles of product)/(moles of 1)] x 100; isolated yield. e) Not detected.

buret through a Molecular Sieves 5A tube. A solution of 1-adamantyl triflate (1) (9.30 mmol) in carbon tetrachloride (57 ml) stabilized by 2,6-di-*t*-butyl-4-methylpyridine (0.03 M) was introduced through a septum cap and magnetically stirred in a  $30 \pm 2$  °C bath to attain thermal equilibrium. On injection of triflic acid (46.3 mmol), rapid CO uptake was observed. After 20 hr the reaction mixture was quenched with an excess amount of cold 5% aq. NaOH and extracted with ether. The neutral compounds from the ether layer were separated with a silica column by using hexane and hexane-ether as eluants to give adamantane (28.5 mmol), 4 (2.19 mmol; 24%), 3 (0.84 mmol; 9%), and 2 (6.52 mmol; 70%) in this sequence.<sup>5</sup> 1-Adamantanecarboxylic acid (2.91 mmol; 31%) was obtained from the aqueous layer in the usual manner.<sup>5</sup> Saponification of 2 in refluxing ethanolic KOH afforded the essentially pure diol 5 in 99% yield. Treatment of 5 with chromic acid<sup>6</sup> gave 3-hydroxy-4-homoadamantanone (6) in 32% yield. The spectral data of the new compounds are summarized in Table 2.<sup>7</sup>

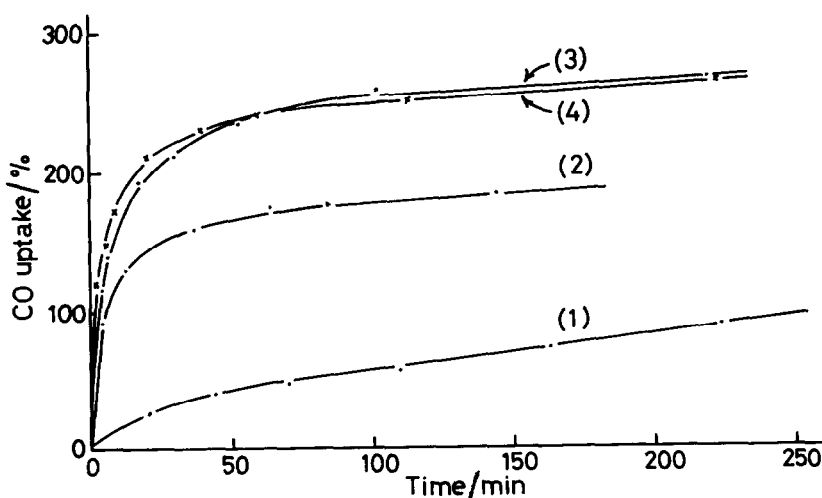
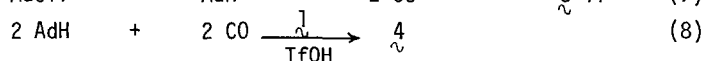
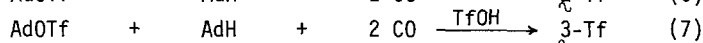
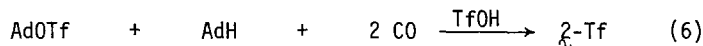


Fig. 1. Plots of CO uptake (mol% on 1) against reaction time. The numbers in parentheses denote the entries in Table 1.



Although we were unable to detect the aldehyde **8** even in early stages of the reaction, its possible existence was supported by an indirect method as follows. When triflic acid (11.3 mmol) was injected to a stirred carbon tetrachloride solution containing **1** (2.33 mmol) and **8** (2.33 mmol) in carbon monoxide atmosphere, a rapid CO uptake was observed. After 20 hr the reaction mixture was worked up as described above to give **2** (0.99 mmol; 43%), **3** (0.65 mmol; 2.8%), and **4** (0.042 mmol; 1.8%).<sup>5,13</sup>

Summing up eq 1 - 5, we can describe the stoichiometries for the formation of the esters **2**-Tf, **3**-Tf, and **4** by eq 6, 7, and 8, respectively. The results that the total product yields exceed 100% on the basis of **1** (entries 3 and 4 in Table 1) should be due to the slow formation of 1-adamantyl cation from adamantane in the presence of triflic acid, which was confirmed by a control experiment.



The mechanistic significance for the combination of 1-adamantyl triflate (**1**), adamantane, and carbon monoxide in the presence of triflic acid is under investigation; the results will be reported in a full paper.

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#### References and notes

1. a) M. A. McKerver, *Chem. Soc. Rev.*, **3**, 479 (1974). b) K. Bott, *Justus Liebigs Ann. Chem.*, **766**, 51 (1972) and previous papers cited therein.
2. K. Takeuchi, T. Moriyama, T. Kineshita, H. Tachino, and K. Okamoto, *Chem. Lett.*, 1395 (1980).
3. For example, 1,2-adamantanediol has been synthesized via seven steps from adamantane; B. D. Cuddy, D. Grant, and M. A. McKerver, *J. Chem. Soc.*, **C**, 1971, 3173.
4. The sole 3,4-bifunctional homoadamantane derivative so far reported is 3-fluoro-4-homoadamantanecarbonitrile; A. E. Sorochinskii, A. M. Aleksandrov, V. F. Gamaleya, and V. P. Kukhar', *Zh. Org. Khim.*, **17**, 1642 (1981).
5. The yields are based on **1**.
6. H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).
7. The ester **4** (mp 245.5-247.5 °C; lit.<sup>8</sup> 247-250 °C) showed <sup>1</sup>H-NMR and IR spectra identical with those of the authentic sample which was prepared from (1-adamantyl)methanol and 1-adamantanecarbonyl chloride.
8. I. Y. Grava, Y. Y. Polis, M. Y. Lidak, É. É. Liepin'sh, V. D. Shatts, I. V. Dipan, M. P. Gavars, and I. P. Sekatsis, *Zh. Org. Khim.*, **17**, 778 (1981).
9. 1-Adamantanecarbonyl cation can also be generated from 1-adamantanecarbonyl chloride and TiCl<sub>4</sub>; T. Sasaki, A. Nakanishi, and M. Ohno, *J. Org. Chem.*, **47**, 3219 (1982).
10. For a mechanistic interpretation, see; G. A. Olah, A. Germain, H. C. Lin, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 2928 (1975). A patent describes the formation of 1-adamantanecarbaldehyde (**8**) from adamantane and carbon monoxide in the presence of AlCl<sub>3</sub>; J. Polis, B. P. Raguel, and É. Liepins, USSR patent 438249 (1976); *Chem. Abstr.*, **86**, 43298w (1976).
11. It is known that a 1-chloroalkyl carboxylate (RCHCl-O-CO-R') is formed in the reaction of an aldehyde (RCHO) and an acyl chloride (R'COCl) in the presence of zinc chloride; e.g., L. H. Ulich and R. Adams, *J. Am. Chem. Soc.*, **43**, 660 (1921).
12. The ester **4** might be formed via acylation of the possible intermediate (1-adamantyl)-methanol in the manner postulated for the formation of ethyl acetate from acetyl cation and isobutane in HF-BF<sub>3</sub>; D. M. Brouwer and A. A. Kiffen, *Rec. Trav. Chim.*, **92**, 689 (1973).
13. Besides, 1-adamantanecarboxylic acid and adamantane were formed.

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