

Formation of adamantan-1-ols by the reactions of adamantanes with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in trifluoromethanesulfonic acid

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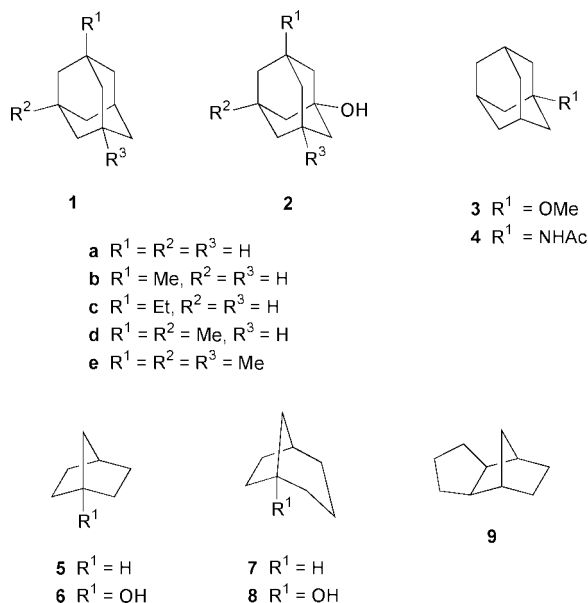
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Adamantanes were treated with DDQ in trifluoromethanesulfonic acid followed by hydrolysis to give adamantan-1-ols in good yields.

Oxidation of adamantanes has been carried out by a variety of reagents such as ozone,¹ peroxy acids,² peroxides,³ lead(IV) acetate in CF₃COOH⁴ and molecular oxygen with a metal catalyst.⁵ These methods normally lead to a mixture of adamantan-1-ols, adamantan-2-ols, adamantan-2-ones and adamantane-1,3-diols via radical processes.

DDQ is a well-known oxidising reagent, especially for reactions involving hydride abstraction from benzylic and allylic positions. But its use in the functionalization of alkanes involving hydride abstraction is not yet known.⁶ The activity of DDQ is enhanced by the addition of protic or Lewis acids such as perchloric acid or BF₃·OEt₂.⁷ If DDQ is activated by a super acid,⁸ we predict that the oxidation of adamantanes is possible in spite of the extremely high oxidation potentials [E_{ox} (adamantane) = 2.72 V vs. SCE⁹].



In this paper, we report that DDQ can abstract a hydride ion from adamantanes (**1**) in trifluoromethanesulfonic acid (TfOH) followed by hydrolysis to give adamantan-1-ols (**2**) exclusively.

In preliminary experiments, the reactivity of adamantane (**1a**) was examined under a variety of conditions. When the reaction was performed in less acidic solvent systems, *i.e.*, CF₃COOH–CH₂Cl₂ (1 : 1) or TfOH–AcOH (1 : 9), no reaction was observed. In TfOH–sulfolane–CH₂Cl₂ (1 : 1 : 1), the

Table 1 The reactions of hydrocarbons **1a–e**, **5** and **7** with DDQ in TfOH^a

Entry	Substrate	<i>t</i> /h	Product	Yield (%) ^b
1	1a	10	2a	89
2	1b	3	2b	86
3	1c	3	2c	88
4	1d	4	2d	85
5	1e	9	2e	86
6	5 ^c	40	6	0
7	7 ^d	40	8	0

^a A mixture of hydrocarbon (1.0 mmol) and DDQ (1.1 mmol) in TfOH (2 cm³) was stirred at room temperature under nitrogen. ^b Isolated yield. ^c 5 mmol of **5** was used. ^d 2 mmol of **7** was used.

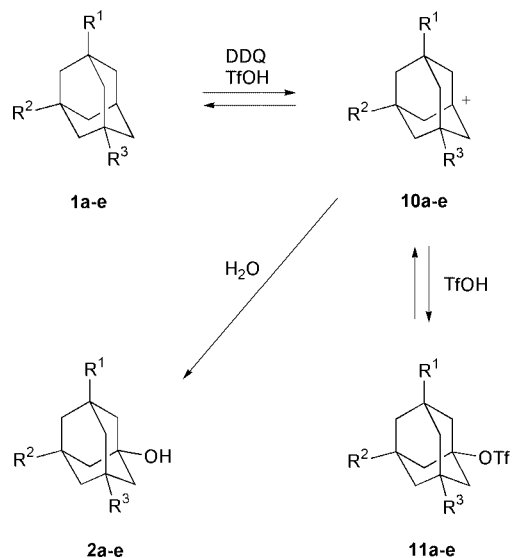
yield of adamantan-1-ol (**2a**) was low (7 h, 30%) because of the production of large amounts of polymeric materials.

When the reaction was performed in TfOH, the best result was obtained. Adamantane **1a** was treated with DDQ in TfOH at room temperature for 10 h under nitrogen followed by hydrolysis to give adamantanol **2a** in 89% yield (Table 1, entry 1). Other adamantane derivatives such as adamantan-2-ols were not detected and DDQH₂ was isolated quantitatively. Without DDQ, the reaction did not occur.

Treatment of the reaction mixture with MeOH afforded 1-methoxyadamantane (**3**) in 54% yield. When CH₃CN was added to the reaction mixture, *N*-(1-adamanty)acetamide (**4**) and adamantanol **2a** were obtained after hydrolysis in 34 and 10% yields, respectively. Similarly, adamantanes **1b–e** reacted with DDQ in TfOH followed by hydrolysis to give adamantanols **2b–e** in good yields (entries 2–7).

Norbornane† (**5**) and bicyclo[3.2.1]octane (**7**) did not react with DDQ in TfOH (entries 6 and 7). In the cases of the other cyclic or acyclic hydrocarbons such as trimethylenenorbornane (**9**), methylcyclopentane, 2-methylundecane and 4-methyldodecane, the reactions proceeded, but only polymeric materials were yielded during the reactions.

We predict that the reactions between adamantanes and DDQ probably proceed by the mechanism as shown in Scheme 1. Hydride transfer from **1a–e** to DDQ activated by TfOH would give adamantyl cations **10a–e**,¹⁰ which are trapped by TfOH to give **11a–e**. Triflates **11a–e** are hydrolysed to **2a–e** by the reaction with water *via* the S_N1 process. The ¹H NMR spectrum of the TfOH solution exhibited the signals at δ 0.90–1.90 (12H, m) and 1.90–2.19 (3H, m), which might be attributed to triflate **11a**. Signals of carbocation **10a**¹⁰ were not detected. These facts indicate that triflate **11a** exists as a major species in TfOH solution. However, attempts to isolate triflate **11a** were unsuccessful. The nucleophilic attack of MeOH and CH₃CN to **10a** would afford **3** and **4**, respectively. The lack of reactivities



Scheme 1

for **5** and **7** could be attributed to the fact that the corresponding bridgehead carbocations are less stable than adamantyl cations.¹¹

Experimental

All products obtained in this study were completely characterized by comparison with authentic samples.

A typical procedure for the reactions of adamantanes **1** with DDQ in TfOH is as follows: to a solution of **1a** (136 mg,

1.0 mmol) in TfOH (2 cm³) was added DDQ (250 mg, 1.1 mmol). After stirring for 10 h at room temperature under nitrogen, the reaction mixture was poured into water (10 cm³) at 0 °C. The mixture was neutralized with K₂CO₃ and extracted with ether. The extracts were washed with water, dried and evaporated. The residue was chromatographed (hexane–acetone = 2 : 1) on silica gel to give **2a** (135 mg, 89%).

Notes and references

† The IUPAC name for norbornane is bicyclo[2.2.1]heptane.

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