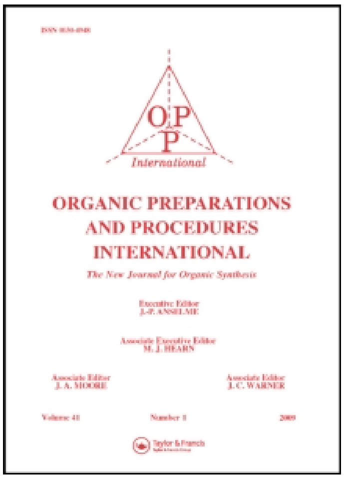

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OXIDATION OF ADAMANTANE TO 1-ADAMANTANOL USING TETRA-N-BUTYLAMMONIUM OXONE

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OPPI BRIEFS

OXIDATION OF ADAMANTANE TO 1-ADAMANTANOL USING TETRA-n-BUTYLAMMONIUM OXONE

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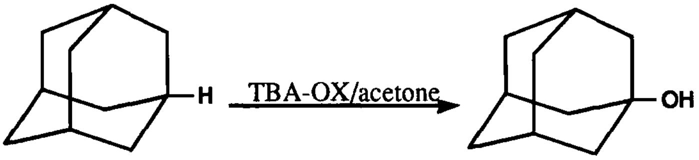
The selective hydroxylation of unactivated hydrocarbons has long presented a major synthetic challenge. The development of reagents has been highlighted by Barton's Fe^{II} and Fe^{III} based oxidative systems (e. g., Gif^{III}, Gif^{IV}, $GoAgg^{I}$, and $GoAgg^{II}$).[1] The application of peroxide based reagents for selective oxidations has been reviewed by Nagata and Saito,[2] and Hill has summarized the present research on functionalization of alkanes.[3]

There have been several reports on the application of dioxiranes for the oxidation of hydrocarbons possessing unactivated C-H bonds, such as adamantane, since the isolation of dimethyldioxirane by Murray and Jeyaraman.[4,5,6] Recently, Mello *et al.* reported the use of "Mello" dioxirane in the selective polyoxy functionalization of adamantane.[7,8] However, the convenient oxidation which involves an *in situ* generation of dioxirane from Oxone® (OX = potassium peroxymonosulfate) and acetone often requires a phase-transfer catalyst for an efficient synthesis.[9] We now report the application of TBA-OX in the oxidation of adamantane to 1-adamantanol by a convenient one-pot synthesis that does not require a separate phase-transfer catalyst. It is anticipated that this approach will prove useful in the large scale oxidation reactions of other hydrocarbons.



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In our study, the reaction of adamantane (**1**) with TBA-OX (22.7% of active agent, Bu_4NHSO_5) was carried out with different mole ratios of starting materials in the presence of sodium bicarbonate. The TBA-OX was prepared by the procedure of Trost *et al.*[10,11] Entry 1 of the Table indicates that TBA-OX does not react with **1** in the absence of acetone and sodium bicarbonate in contrast to sulfides which react to give sulfones. Entries 2 and 3 also show no significant reaction in the absence of water and bicarbonate. However, in the presence of sodium bicarbonate and water

(Entry 4), a 48% conversion of **1** to **2** was achieved. This is similar to the observation reported by Suryawanshi and Fuchs in the oxidation of dienyl ethers to γ-hydroxy enones using Oxone® and sodium bicarbonate in aqueous tetrahydrofuran.[12] When the oxidation of adamantane with TBA-OX and sodium bicarbonate was repeated in the presence of excess acetone, complete conversion of **1** to **2** was observed (Entry 8). However, when a 1:1.5 ratio of active agent and acetone was used in these experiments, a decrease in the conversion was observed (Entries 5 and 7). A comparison of entries 5 and 7 with 6 and 8 indicates that the use of excess acetone has a significant effect on the reaction. The requirement of excess acetone for maximum conversion suggests that the most active oxidant is *in situ* generated dimethyldioxirane. Similar enhancement of the reactivity of potassium oxone by acetone was observed in the oxidation of olefins to epoxides.[13,14]

TABLE. Hydroxylation of Adamantane by TBA-Oxone and Acetone

Entry	1: Active agent ratio	Time	Active agent: Acetone ratio	Conversion[a]
1	1:10	21 h	no acetone[b]	no reaction
2	1:10	21 h	1:52[c]	no reaction
3	1:10	21 h	1:52[d]	no reaction
4	1:10	21 h	no acetone[e]	48%
5	1:4	4 days	1:1.5[f]	30%
6	1:4	4 days	1:52[g]	34%
7	1:10	21 h	1:1.5[f]	55%
8	1:10	21 h	1:52[g]	100%
9	1:20	21 h	1:52[g]	100%

a) The conversion of **1** to **2** was determined by ^{1}H NMR at 300 MHz. b) TBA-OX and **1** were stirred in CH_2Cl_2 in the absence sodium bicarbonate and water. c) Procedure A was followed without water. d) Procedure A was followed without $NaHCO_3$. e) Procedure B was followed without acetone. f) Procedure B was followed. g) Procedure A was followed.

When a 1:4 mole ratio of **1** and TBA-OX was used, a 34% conversion of **1** was obtained after four days stirring at ambient temperature. But, when a mole ratio of 1:10 was used, 100% conversion was achieved after 21 hrs. Complete conversion of **1** to **2** was also observed when a 20-fold excess of TBA-OX was used. A large scale reaction showed 80% conversion after three days with mechanical stirring. In none of these cases was the presence of either adamantan-1,3,5-triol or adamantan-1,3,5,7-tetraol observed in ^{1}H NMR. However, the presence of 2-adamantanol or 2-adamantanone in very small amounts in the product mixture has not been excluded.

We are currently exploring the use of TBA-OX in the oxidation of hydrocarbons with the exclusion of acetone.

EXPERIMENTAL SECTION

All reagents were purchased from Aldrich Chemical Co. and were used without any further purification. The ^{1}H NMR obtained from Bruker AM300 spectrometer at 300 MHz was used in the identification of product and determination of percentage of conversion.

Oxidation of Adamantane

Procedure A (Entry 9).- In a typical reaction, a mixture consisting of sodium bicarbonate (2.37 g, 0.028 mol), 10 mL water, acetone (19.2 mL, 0.26 mol) and **1** (34 mg, 0.25 mmol) was placed in a 100 mL single neck round bottom flask, equipped with a stir bar, a Claisen adapter, a condenser, an addition funnel and a bubbler. To this mixture, a solution of TBA-OX (7.81 g, 5 mmol) in 25 mL methylene chloride, was added dropwise for a period of 1.5 hr. The resulting mixture was stirred in the dark at ambient temperature for 21 hrs. The volatile components were removed on a rotatory evaporator, and the residue was fractionated in a 1:1 mixture of ether and water. The ethereal layer was separated, dried over anhydrous magnesium sulfate, and the solvent was removed on a rotatory evaporator, to yield 30 mg of **2** as a white solid (79% yield), mp. (in a sealed tube, uncorrected) 238-240° (subl). The product was identified by comparing its ^{1}H NMR with that of an authentic sample (purchased from Pfaltz and Bauer, Inc.), mp. (in a sealed tube, uncorrected) 238-240° (subl).

In a larger scale reaction, a mixture consisting of sodium bicarbonate (17.4 g, 0.207 mol), 74 mL water, acetone (141 mL, 1.93 mol) and **1** (0.25 g, 1.84 mmol) was placed in a 1 L three-neck round bottom flask, equipped with a mechanical stirrer, condenser, addition funnel and a bubbler. To this mixture, a solution of TBA-OX (57.43 g, 0.037 mol) in 184 mL methylene chloride, was added dropwise over a period of 5.5 hrs. The resulting mixture was stirred at ambient temperature for three days in the dark. The volatile components were removed on a rotary evaporator, and the residue was fractionated in a 1:1 mixture of ether and water. The ethereal layer was separated, dried over anhydrous magnesium sulfate and the solvent removed on a rotary evaporator. The product was isolated by silica gel column with hexane and ether as eluents. The product (**2**), mp. 238-240° (subl), was obtained from the ether fraction in 70% yield (195 mg).

Procedure B (Entry 7).- A mixture consisting of sodium bicarbonate (1.18 g, 0.014 mol), 5 mL water, 6.25 mL methylene chloride, acetone (275 mL, 3.75 mmol) and **1** (34 mg, 0.25 mmol) was placed in 50 mL single neck round bottom flask, equipped with a stir bar, a condenser, a Claisen adapter, an addition funnel and a bubbler. To this mixture, a solution of TBA-OX (3.91 g, 2.5 mmol) in 6.25 mL methylene chloride, was added dropwise for a period of 1.5 hr. The resulting mixture was stirred in the dark at ambient temperature for 21 hrs. Workup and isolation was as described for procedure A.

Caution: Although no explosion was experienced in our laboratories, tetra-*n*-butylammonium oxone should be treated as a potential explosive.

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