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# Oxidation of Adamantane with $H_2O_2$–$CF_3COCF_3 \cdot 1.5\,H_2O$ in the Presence of $VO(acac)_2$

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**Abstract**—The system hydrogen peroxide–hexafluoroacetone sesquihydrate effectively oxidizes adamantane in the presence of $VO(acac)_2$ to afford 64% of adamantan-1-ol in *tert*-butyl alcohol or 76% of adamantan-2-one in a mixture of acetic acid with pyridine.

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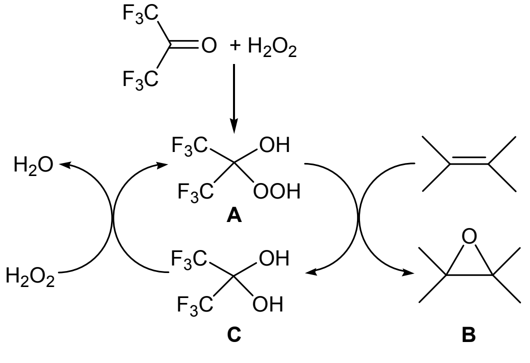
Adamantane and its homologs are oxidized more readily than saturated aliphatic and alicyclic hydrocarbons. Oxidative functionalization of adamantane has been accomplished using a broad series of oxidants, including oxygen, hydrogen peroxide, hydroperoxides, peroxyacids, HOCl, HOBr, NaOCl, iodosobenzene, and 2,6-dichloropyridine *N*-oxide in combination with metal complex catalysts based on Co, Mn, Mo, Fe, Zn, Pd, and Pt [1–5]. The oxidation of adamantane with these reagents was usually characterized by low conversion and selectivity, and mixtures of adamantan-1-ol, adamantan-2-ol, and adamantan-2-one were obtained. This is related to the radical mechanism of the reaction involving the system oxidant–metal complex [1]. For example, the conversion of adamantane in the oxidation with the most environmentally benign oxidant, hydrogen peroxide, in the presence of iron compounds did not exceed 13% [5].

A mixture of hydrogen peroxide with hexafluoroacetone sesquihydrate showed a high activity in epoxidation of olefins, oxidation of aldehydes to carboxylic acids, and oxidation of sulfides and amines to the corresponding sulfoxides and amine oxides [6]. The high oxidizing power of the system $H_2O_2$–$(CF_3)_2CO \cdot 1.5\,H_2O$ may be rationalized as follows. Highly electrophilic perfluoroacetone reacts with hydrogen peroxide to produce hydroperoxide **A** which oxidizes unsaturated substrate to give epoxide **B** and hydrate **C**. The reaction of the latter with hydrogen peroxide regenerates hydroperoxide **A**, thus resuming the catalytic cycle [7] (Scheme 1).

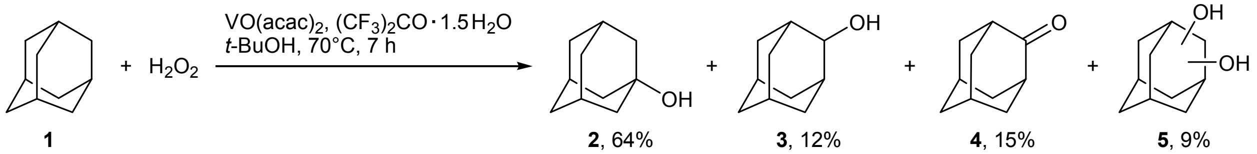
There are no published data on the use of $H_2O_2$–$(CF_3)_2CO \cdot 1.5\,H_2O$ for the oxidation of saturated hydrocarbons. In this work we tried this oxidizing system for the oxidative functionalization of adamantane in the presence of vanadium complexes.

The conversion of adamantane largely depends on the solvent nature, temperature, catalyst, and rate of addition of $H_2O_2$–$(CF_3)_2CO \cdot 1.5\,H_2O$. An appreciable reaction rate was achieved at 40°C, and the maximum conversion of adamantane (Table 1, run no. 20) was obtained at 70°C. Blank experiments (without adamantane) showed that the oxidant strongly decomposes at 70°C in the presence of $VO(acac)_2$. According to the iodometric titration data, after 10 min the concentration of active oxygen decreases by almost an order of magnitude. Therefore, the reaction was carried out by gradually adding $H_2O_2$–$(CF_3)_2CO \cdot 1.5\,H_2O$ mixture to the reaction mixture containing adamantane, catalyst, and solvent, preliminarily heated to 40–70°C. Among

**Scheme 1.**



**Scheme 2.**



the solvents tested ($CH_2Cl_2$, $CHCl_3$, EtOH, BuOH, *t*-BuOH), *tert*-butyl alcohol turned out to be the best one, since it was not involved in side reactions. Moreover, *tert*-butyl alcohol is miscible with 35% aqueous hydrogen peroxide, and it readily dissolves adamantane (**1**) and $VO(acac)_2$.

The reactions were carried out at ratios **1**–$H_2O_2$–$(CF_3)_2CO \cdot 1.5H_2O$–$VO(acac)_2$ of 100:(500–1000):(3–7):(100–250) at 40, 60, and 70°C, the reaction time ranging from 4 to 7.5 h. Under the optimal conditions (70°C, 7 h), the major product was adamantan-1-ol (**2**, yield 64%), and the conversion of adamantane (**1**) was 99%. The reaction mixtures also contained ~30% of by-products represented mainly by adamantan-2-ol (**3**), adamantan-2-one (**4**), and isomeric dihydroxyadamantanes **5**, which were identified by GC/MS (Scheme 2). Thus, the oxidation of adamantane was not selective, and the ratio **2**:**3**:**4**:**5** was ~2:1:1:0.5 (Table 1, run nos. 18–20). In the absence of a catalyst, the conversion of **1** was 77% (run no. 8), and the ratio **2**:**3** was 2:1. If no $(CF_3)_2CO \cdot 1.5H_2O$ was added, the conversion of adamantane did not exceed 44% (run no. 7).

Additional experiments showed that the results of adamantane oxidation are largely determined by the solvent nature. In the oxidation of **1** in acetic acid–pyridine, the major product was adamantan-2-one (**4**) which was formed with a selectivity of 76%, and the conversion of adamantane reached 95% (Table 2, run no. 4). In the absence of $(CF_3)_2CO \cdot 1.5H_2O$, the conversion of **1** was as low as 49% (run no. 2), while in

**Table 1.** Oxidation of adamantane (**1**) with $H_2O_2$–$(CF_3)_2CO \cdot 1.5H_2O$ in *tert*-butyl alcohol

| Run no. | Ratio **1**–$H_2O_2$–$(CF_3)_2CO \cdot 1.5H_2O$–$VO(acac)_2$ | Temperature, °C | Reaction time, h | Conversion of **1**, % | Product composition, % | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | **2** | **3** | **4** | **5** |
| 1 | 100:500:50:0 | 40 | 7 | 0 | – | – | – | – |
| 2 | 100:500:50:0 | 60 | 7 | 5 | 56 | 44 | – | – |
| 3 | 100:500:50:0 | 70 | 7 | 18 | 61 | 25 | 14 | – |
| 4 | 100:500:100:0 | 70 | 7 | 32 | 64 | 25 | 11 | – |
| 5 | 100:500:200:0 | 70 | 7 | 13 | 64 | 19 | 17 | – |
| 6 | 100:1000:100:0 | 70 | 7 | 40 | 69 | 31 | – | – |
| 7 | 100:1000:0:7 | 70 | 7 | 44 | 68 | 13 | 13 | 6 |
| 8 | 100:1000:250:0 | 70 | 7 | 77 | 63 | 37 | – | – |
| 9 | 100:1000:250:1 | 70 | 7 | 83 | 65 | 12 | 14 | 9 |
| 10 | 100:1000:100:3 | 70 | 7 | 58 | 65 | 14 | 15 | 6 |
| 11 | 100:1000:250:3 | 70 | 7.5 | 91 | 66 | 14 | 15 | 5 |
| 12 | 100:1000:250:5 | 70 | 7 | 86 | 61 | 14 | 17 | 8 |
| 13 | 100:500:250:7 | 60 | 7 | 47 | 66 | 13 | 16 | 5 |
| 14 | 100:500:250:7 | 70 | 7 | 76 | 62 | 13 | 15 | 10 |
| 15 | 100:1000:100:7 | 40 | 7 | 19 | 66 | 21 | 13 | – |
| 16 | 100:1000:100:7 | 70 | 3 | 74 | 62 | 18 | 12 | 8 |
| 17 | 100:1000:100:7 | 70 | 7 | 88 | 60 | 14 | 15 | 11 |
| 18 | 100:1000:250:7 | 70 | 5 | 90 | 68 | 14 | 14 | 4 |
| 19 | 100:1000:250:7 | 70 | 7 | 91 | 65 | 14 | 16 | 5 |
| 20 | 100:1000:500:7 | 70 | 7.5 | 99 | 64 | 12 | 15 | 9 |

**Table 2.** Oxidation of adamantane (**1**) with $H_2O_2$–$(CF_3)_2CO \cdot 1.5H_2O$ in a mixture of acetic acid with pyridine

| Run no. | Ratio **1**–$H_2O_2$–$(CF_3)_2CO \cdot 1.5H_2O$–AcOH–Py–$VO(acac)_2$ | Temperature, °C | Reaction time, h | Conversion of **1**, % | Product composition, % | | |
|---|---|---|---|---|---|---|---|
| | | | | | **2** | **3** | **4** |
| 1 | 100:1000:500:300:0:7 | 70 | 7 | 87 | 73 | 9 | 18 |
| 2 | 100:1000:2500:0:3500:7 | 60 | 7 | 49 | 19 | – | 81 |
| 3 | 100:1000:50:2500:0:7 | 60 | 7 | 56 | 52 | – | 48 |
| 4 | 100:1000:50:2500:3500:7 | 60 | 7 | 95 | 24 | – | 76 |
| 5 | 100:1000:100:2500:3500:7 | 70 | 8 | 37 | 37 | – | 63 |

the absence of pyridine, the substrate conversion decreased to 56% (run no. 3), and the reaction mixture contained adamantan-1- and -2-yl acetates (25%) which were identified by GC/MS.

Study of the kinetics of blank experiments (without adamantane) showed that the rate of generation of active oxygen depends on the temperature and catalyst: the higher the temperature, the higher the rate of oxygen liberation. In the absence of a catalyst, the rate of decomposition of $H_2O_2$ and $(CF_3)_2C(OH)(OOH)$ (**A**) was 3–5 times lower even at elevated temperature. Despite intense generation of active oxygen in the presence of $VO(acac)_2$, the conversion of adamantane (**1**) attained 99%; therefore, the rate of oxidation of adamantane is higher than the rate of decomposition of the oxidants [$H_2O_2$ and $(CF_3)_2C(OH)(OOH)$].

Gaseous reaction products contained oxygen and traces of hydrogen fluoride, indicating partial hydrolysis of hexafluoroacetone. No other gaseous hexafluoroacetone decomposition products were detected. The use of such metal complexes as $Cr(acac)_3$, $Mn(acac)_3$, $Ni(acac)_2$, $Fe(acac)_3$, $Mo(CO)_6$, and $W(CO)_6$ gave no satisfactory results.

Thus, the system hydrogen peroxide–hexafluoroacetone sesquihydrate in the presence of $VO(acac)_2$ is efficient for the oxidation of adamantane. The reaction direction depends on the solvent. The oxidation in *tert*-butyl alcohol gives mainly adamantan-1-ol (**2**, 64%), whereas adamantan-2-one (**4**, 76%) is formed as the major product in acetic acid–pyridine.

## EXPERIMENTAL

The IR spectra were recorded in KBr or mineral oil on a Bruker Vertex 79V spectrometer. The $^1H$ and $^{13}C$ NMR spectra were measured on a Bruker Avance-400 spectrometer at 400.13 and 100.62 MHz, respectively, using $CDCl_3$ as solvent and tetramethylsilane as reference. The mass spectra were recorded on a Shimadzu GCMS-QP2010 Ultra instrument (Supelco PTE-5 capillary column, 60 m × 0.25 mm, carrier gas helium, oven temperature programming from 40 to 280°C at a rate of 8 deg/min, injector temperature 260°C, ion source temperature 200°C; electron impact, 70 eV). Chromatographic analysis was performed with a Carlo Erba GC 6000 Vega Series 2 chromatograph (3-m steel column packed with 15% PEG-6000 on Chromaton N-AW-HMDS; oven temperature programming from 50 to 180°C at a rate of 8 deg/min; carrier gas helium, flow rate 47 mL/min). The elemental compositions were determined with a Carlo Erba 1108 analyzer. Gas mixtures were analyzed with a Thermo Finnigan DSQ II GC/MS system; a 0.5-mL sample was injected with a split ratio of 1:100; isothermal mode, 50°C; the mass spectra were recorded in the range from 15 to 200 a.m.u.

**Adamantan-1-ol (2).** A reaction flask was charged with 1 mmol of adamantane (**1**), 0.14 mmol of $VO(acac)_2$, and 43 mmol of *tert*-butyl alcohol. The solution was heated to 70°C, and a mixture of 10 mmol of 32% hydrogen peroxide and 2.5 mmol of hexafluoroacetone sesquihydrate was added dropwise from a dropping funnel over a period of 5 h. The mixture was cooled to 20°C, washed with water, and extracted with ethyl acetate (3 × 5 mL). The extract was evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel using hexane–ethyl acetate (first 9:1 and then 7:3) as eluent. Yield 66%, mp 246–247°C. IR spectrum, ν, $cm^{-1}$: 3600 (O–H), 1150 (C–O). $^1H$ NMR spectrum, δ, ppm: 1.65 m (12H, 2-H, 4-H, 6-H, 8-H, 9-H, 10-H), 2.10 m (3H, 3-H, 5-H, 7-H), 2.45 s (1H, OH). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 67.90 ($C^1$), 45.32 ($C^2$, $C^8$, $C^9$), 36.15 ($C^4$, $C^6$, $C^{10}$), 30.85 ($C^3$, $C^5$, $C^7$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 152 (24) $[M]^+$, 29 (7), 39 (10), 41 (12), 43 (15), 53 (5), 55 (7), 67 (5), 77 (7), 79 (5), 94 (14), 95 (100), 96 (7), 109 (5). Found, %: C 78.67; H 10.17. $C_{10}H_{16}O$. Calculated, %: C 78.89; H 10.59. *M* 152.2364.

**Adamantan-2-one (4).** A reaction flask was charged with 1 mmol of adamantane (**1**), 0.14 mmol of $VO(acac)_2$, 25 mmol of acetic acid, and 35 mmol of pyridine. The solution was heated to 60°C, and a mixture of 10 mmol of 32% hydrogen peroxide and 0.5 mmol of hexafluoroacetone sesquihydrate was added dropwise from a dropping funnel over a period of 5 h. The mixture was cooled to 20°C, washed with brine, and extracted with ethyl acetate (3 × 5 mL). The extract was evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel using hexane–ethyl acetate (first 9 : 1 and then 7 : 3) as eluent. Yield 70%, mp 256–257°C (sublimes); published data [8]: mp 256–258°C. $^{13}C$ NMR spectrum, $\delta_C$, ppm: 27.64 ($C^5$, $C^7$), 36.31 ($C^6$), 39.20 ($C^4$, $C^8$, $C^9$, $C^{10}$), 46.92 ($C^1$, $C^3$), 216.59 ($C^2$). Found, %: C 79.78; H 9.12. $C_{10}H_{14}O$. Calculated, %: C 79.95; H 9.39.

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