

## Selective Rhodium-catalysed Oxidation of Alkanes to Alkyl Esters with Peracids

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Saturated hydrocarbons are selectively transformed into the corresponding alkyl trifluoroacetates in good yields by treatment with hydrogen peroxide in trifluoroacetic acid in the presence of Rh salts at room temperature.

The C–H bond activation of hydrocarbons, especially alkanes, by transition metal complexes under mild conditions is one of the important targets of recent chemistry. Thus, as to the oxidative activation, considerable efforts have so far been paid on the liquid-phase oxidation of alkanes with various oxidants including molecular oxygen catalysed by a variety of transition metal complexes.<sup>1–3</sup> Nevertheless, to our knowledge, there are no reports on rhodium-catalysed oxidative C–H activation of alkanes, although Rh-catalysed carbonylation of alkanes is known.<sup>4</sup> Previously we have reported that  $\mu_3$ -oxotrirhodium acetate complex  $[\text{Rh}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]\text{OAc}$  (abbreviated as  $\text{Rh}_3\text{O}$ ) and  $\text{Rh}_2(\text{OAc})_4$  worked as homogeneous catalysts for the allylic oxidation of alkenes with  $\text{Bu}^t\text{O}_2\text{H}$ .<sup>5</sup> Further studies revealed that various rhodium catalysts including these were quite effective for alkane oxidation to alkyl esters and/or ketones with peracids, typical results of which are reported here.

A mixture of cyclohexane **1** (10 mmol), Rh salt (0.033–0.1 mmol), peracetic acid (30 mmol), and acetic acid (20 ml) was stirred at 25 °C for 2 days. After the usual work-up procedure (addition of aq. NaCl, extraction with  $\text{CH}_2\text{Cl}_2$ , washing with aq.  $\text{NaHCO}_3$ , drying over  $\text{Na}_2\text{SO}_4$ ) GLC analysis of the extract revealed the presence of cyclohexanone as a major product together with cyclohexanol and cyclohexyl acetate. Without the rhodium complex or the oxidant the reaction hardly occurred. The reaction proceeded fairly slowly and the turnover number was around 7–36 per catalyst and 6–12 per rhodium metal. Among Rh salts examined,  $\text{Rh}_3\text{O}$  was revealed to be the most effective, followed by various rhodium compounds such as tris(acetylacetonato)rhodium  $[\text{Rh}(\text{acac})_3]$ ,  $[\text{RhCl}(\text{CO})_2]_2$ , Wilkinson's complex  $[\text{RhCl}(\text{PPh}_3)_3]$  and the rhodium acetate dimer  $[\text{Rh}_2(\text{OAc})_4]$ . Several oxidising agents other than peracetic acid such as  $\text{H}_2\text{O}_2$ ,  $\text{Bu}^t\text{O}_2\text{H}$ , *m*-CPBA were examined and eventually peracetic acid was revealed to be the best for this reaction (Fig. 1).

Next, we looked for a more effective reaction system by changing the combination of the oxidant and the solvent, and found that a mixture of  $\text{H}_2\text{O}_2$  and trifluoroacetic acid (TFA) was very efficient, a similar system of which has been employed for  $\text{Pd}^{2+}$ ,  $\text{Co}^{3+}$  and  $\text{Mn}^{2+}$ -catalysed and -mediated alkane oxidation.<sup>2</sup> Thus, in the oxidation of cyclohexane, the product yield as well as the turnover number increased remarkably and the selectivity for the ester, cyclohexyl trifluoroacetate, became quite high. As shown in Table 1, any rhodium salts examined were revealed to be quite effective. The oxidation catalysed by  $\text{Rh}_3\text{O}$  in the presence of 6-*tert*-butyl-*o*-cresol or *p*-benzoquinone as a radical scavenger took place without the decrease of product yield, showing an ionic nature of the reaction. This  $\text{Rh}_3\text{O}$  catalysed oxidation system could be applied well to the oxidation of adamantane **4** and *n*-octane **10** under similar conditions. The distribution of the oxidised products from **4** and **10** indicates that the reactivity of C–H bonds of alkane is in the order of tertiary > secondary > primary. This result is similar to that observed in alkane oxidation with transition metal (Ru, Fe, Cu) salts–aldehyde– $\text{O}_2$  system,<sup>3</sup> but not to that obtained with Barton's Gif system where the *sec* C–H reacted faster than the *tert* one (*sec*:*tert* = 1.14–1.16).<sup>6</sup> Other transition metal salts of group VIII (Fe, Ru, Pd, Pt) also worked as catalysts (Table 1), though slightly less effectively than Rh salts.

We have no experimental evidence to propose a clear-cut reaction pathway. However, on the basis of experimental findings such as the reactivity order tertiary > secondary > primary as well as an ionic nature of the reaction, we propose the reaction pathway shown in Scheme 1. A highly reactive oxorhodium species (**b**) similar to the so far proposed oxoruthenium(IV)<sup>3c</sup> and oxoiron(IV)<sup>7</sup> species is formed by heterolytic cleavage of the O–O bond of the initially produced (pertrifluoroacetoxy)rhodium species (**a**). Then, the hydrogen abstraction from alkane with **b** and the oxygen transfer to

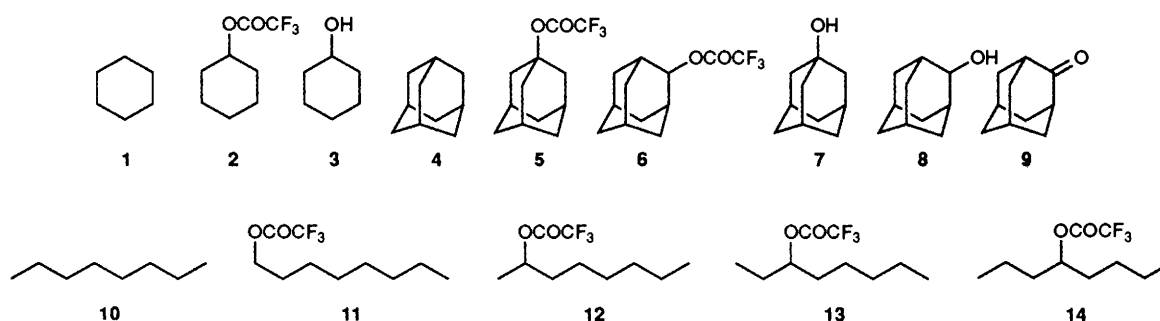
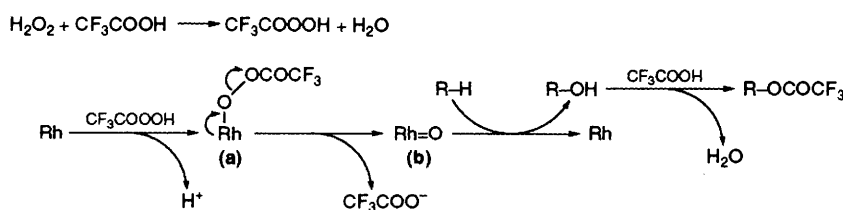


Fig. 1



Scheme 1

**Table 1** Transition metal-catalysed oxidation of alkanes with H<sub>2</sub>O<sub>2</sub> in TFA<sup>a</sup>

Entry	Alkane/mmol	Catalyst/mmol <sup>b</sup>	Products (% yield) <sup>c</sup>	Turnover no. <sup>d</sup>	
1	<b>1</b> (10)	Rh <sub>3</sub> O (0.0033)	<b>2</b> (62.2)	<b>3</b> (1.5)	1911
2	<b>1</b> (10)	Rh(acac) <sub>3</sub> (0.01)	<b>2</b> (64.1)	<b>3</b> (1.5)	656
3	<b>1</b> (10)	RhCl(PPh <sub>3</sub> ) <sub>3</sub> (0.01)	<b>2</b> (63.6)	<b>3</b> (2.5)	661
4	<b>1</b> (10)	RhCl <sub>3</sub> ·3H <sub>2</sub> O (0.01)	<b>2</b> (62.5)	<b>3</b> (1.6)	641
5	<b>1</b> (10)	Rh <sub>2</sub> (OAc) <sub>4</sub> (0.005)	<b>2</b> (64.6)	<b>3</b> (1.6)	1324
6 <sup>e</sup>	<b>4</b> (5)	Rh <sub>3</sub> O (0.017)	<b>5</b> (7.2) <b>6</b> (4.0) <b>7</b> (33.6) <b>8</b> (0.3) <b>9</b> (3.0)		144
7 <sup>f</sup>	<b>10</b> (5)	Rh <sub>3</sub> O (0.017)	<b>11</b> (trace) <b>12</b> (9.9) <b>13</b> (10.0) <b>14</b> (11.0)		93
8	<b>1</b> (10)	Pd(OAc) <sub>2</sub> (0.01)	<b>2</b> (37.5)	<b>3</b> (0.7)	382
9	<b>1</b> (10)	RuCl <sub>3</sub> (0.01)	<b>2</b> (57.5)	<b>3</b> (1.4)	589
10	<b>1</b> (10)	H <sub>2</sub> PtCl <sub>6</sub> ·6H <sub>2</sub> O (0.01)	<b>2</b> (48.7)	<b>3</b> (1.3)	500
11	<b>1</b> (10)	FeCl <sub>3</sub> ·6H <sub>2</sub> O (0.01)	<b>2</b> (53.9)	<b>3</b> (1.3)	552

<sup>a</sup> Carried out by using alkane, 30% H<sub>2</sub>O<sub>2(aq)</sub> (3 mol equiv. to alkane), and a catalyst in TFA (20 ml) at 25 °C for 1 day. <sup>b</sup> Rh<sub>3</sub>O = [Rh<sub>3</sub>O(OAc)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]OAc. <sup>c</sup> Determined by GLC on the basis of alkane. All authentic samples of trifluoroacetates were prepared from the corresponding commercial alcohols. <sup>d</sup> Per catalyst. <sup>e</sup> A mixture of TFA (10 ml) and AcOH (20 ml) was used as solvent. At 25 °C for 2 days. <sup>f</sup> At 25 °C for 2 days.

alkane from **b** occur simultaneously to give the corresponding alcohol. The produced alcohol, as we confirmed separately, is subsequently converted into the trifluoroacetate.

Received, 8th September 1993; Com. 3/05401B

## References

- For examples, D. H. R. Barton, M. J. Gastiger and W. B. Motherwell, *J. Chem. Soc., Chem. Commun.*, 1983, 41; D. H. R. Barton, F. Halley, N. Ozbalik, M. Schmitt, E. Young and G. Balavoine, *J. Am. Chem. Soc.*, 1989, **111**, 7144; M. Lin and A. Sen, *J. Am. Chem. Soc.*, 1992, **114**, 7307; N. Kitajima, M. Ito, H. Fukui and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1991, 102; M. Bressan, A. Morvillo and G. Romanello, *J. Mol. Catal.*, 1992, **77**, 283.
- E. Gretz, T. F. Oliver and A. Sen, *J. Am. Chem. Soc.*, 1987, **109**, 8109; L.-C. Kao, A. C. Hutson and A. Sen, *J. Am. Chem. Soc.*, 1991, **113**, 700; M. N. Vargaftik, I. P. Stolarov and I. I. Moiseev, *J. Chem. Soc., Chem. Commun.*, 1990, 1049.
- (a) S. Murahashi, Y. Oda and T. Naota, *J. Am. Chem. Soc.*, 1992, **114**, 7913; (b) S. Murahashi, Y. Oda, T. Naota and N. Komiya, *J. Chem. Soc., Chem. Commun.*, 1993, 139; (c) S. Murahashi, Y. Oda, T. Naota and T. Kuwabara, *Tetrahedron Lett.*, 1993, **34**, 1299.
- T. Sakakura, K. Sasaki, Y. Tokunaga, K. Wada and M. Tanaka, *Chem. Lett.*, 1988, 155; T. Sakakura and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1987, 758.
- S. Uemura and S. R. Patil, *Tetrahedron Lett.*, 1982, **23**, 4353; S. Uemura and S. R. Patil, *Chem. Lett.*, 1982, 1743.
- D. H. R. Barton, J. Boivin, N. Ozbalik and K. M. Schwartzen-truber, *Tetrahedron Lett.*, 1985, **26**, 447.
- For example, J. F. Bartoli, O. Brigaud, P. Battioni and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1991, 440 and references cited therein.