Pergamon

Tetrahedron Letters 39 (1998) 4359–4362

TETRAHEDRON LETTERS

Ruthenium(II)–Bipyridine Anchored Montmorillonite–Catalyzed Oxidation of Aromatic Alkenes with *tert*-Butyl Hydroperoxide

Takahiro Nishimura, Tomoaki Onoue, Kouichi Ohe, Jun-ichi Tateiwa, and Sakae Uemura*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

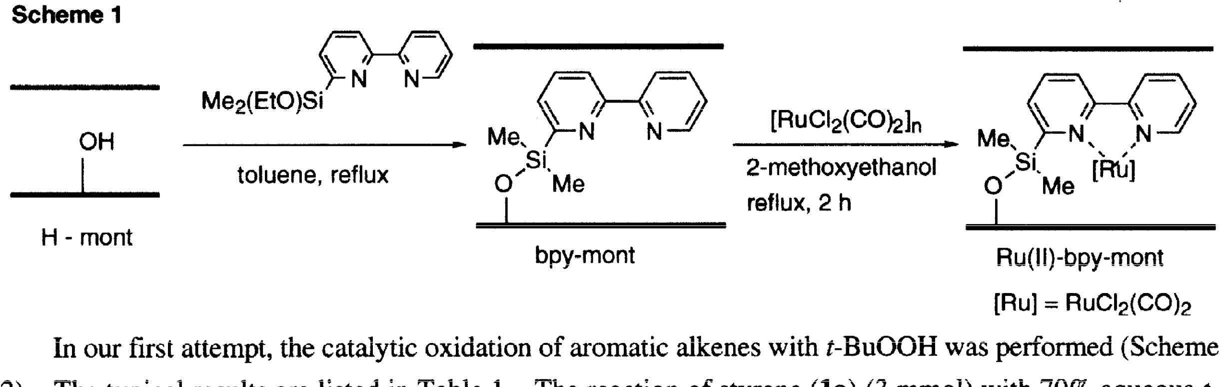
Received 2 March 1998; accepted 13 April 1998

Abstract: *Bipyridylsilylated montmorillonite (abbreviated as bpy-mont) is prepared from H-montmorillonite and 6-(ethoxydimethylsilyl)-2,2'-bipyridine. Treatment of the bpy-mont with $[RuCl_2(CO)_2]_n$ affords a novel clay catalyst including Ru(II)-bpy. The oxidation of aromatic alkenes with tert-BuOOH in the presence of the catalyst and Et_3N mainly produces vic-bis(tert-butyldioxy)alkanes. A similar oxidation of 2,3-dimethyl-1,3-butadiene affords 1,4- and 1,2-bis(tert-butyldioxy)alkenes. In the absence of Et_3N the oxidation of 1,1-diphenylethylene gives 2-tert-butyldioxy-1-hydrodioxy-1,1-diphenylethane as a major product. This catalyst is easily separated after the reactions and can be reused for oxidation.*

Smectite clays such as montmorillonite are currently receiving considerable attention as benign and reusable Lewis and Brønstead acid catalysts.[1] Modification by exchanging a cation (H^+ or Na^+) between the layers for metals or by anchoring ligands containing metals provides the new catalytic use of clays. Several types of the cation-exchanged clay hitherto have been reported to exhibit remarkable catalytic activity for some organic reactions.[1,2] On the other hand, the utility of the clay anchored with organic ligand which supports transition metals has been restricted to some examples [1,3] and further elaboration in this field is waited for widening the utility of such clays in organic synthesis. Recently, ruthenium-catalyzed oxidation has been extensively studied from a viewpoint of mimicking cytochrom P-450 system and has proved to be useful for oxidative transformation of organic molecules.[4] We report herein the synthesis of a new clay catalyst anchored with bipyridine ligand for metals and its application to oxidation of aromatic alkenes using ruthenium embedded in it.[5] The results using homogeneous ruthenium catalyst which has been scarcely studied in oxidation of alkenes are also recorded.

The treatment of H-montmorillonite (H-mont) with 6-(ethoxydimethylsilyl)-2,2'-bipyridine[6] in toluene under reflux gave bipyridylsilylated montmorillonite (abbreviated as bpy-mont). The reaction of the bpy-mont with $[RuCl_2(CO)_2]_n$[7] afforded Ru(II) embedded bpy-mont [Ru(II)-bpy-mont].[8] The procedure for preparation is shown in Scheme 1.

Scheme 1

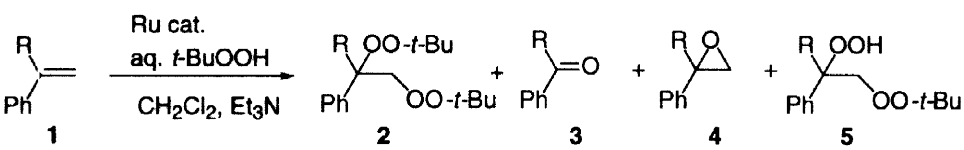


In our first attempt, the catalytic oxidation of aromatic alkenes with *t*-BuOOH was performed (Scheme 2). The typical results are listed in Table 1. The reaction of styrene (**1a**) (3 mmol) with 70% aqueous *t*-BuOOH (5 equiv) in CH_2Cl_2 at 25 °C for 48 h in the presence of Ru(II)-bpy-mont (0.0015 mmol) and

0040-4039/98/$19.00 © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(98)00795-3

Et_3N (0.1 mL) afforded 1,2-bis(*tert*-butyldioxy)-1-phenylethane (**2a**) (30%) and benzaldehyde (13%) (Table 1, entry 1). The reaction of α-methylstyrene (**1b**) and 1,1-diphenylethylene (**1c**) gave the corresponding 1,2-bis(*tert*-butyldioxy) adducts **2b** and **2c** in 33% and 59% yields, respectively (entries 2 and 3).[9] Epoxides **4** which were minor products are not intermediates leading to **2a**-**2c**, because conversion of styrene oxide (**4a**) to **2a** was not observed under the identical conditions. Similarly, homogeneous $RuCl_2(bpy)(CO)_2$-,[10] $RuCl_2(bpy)_2{\cdot}2H_2O$-,[11] and $[Ru(CO)_2Cl_2]_n$-catalyzed oxidation of **1c** under the same conditions afforded **2c** in 69%, 71% and 63% yields, respectively (entries 4, 5, and 6). In the absence of catalyst the rate of oxidation was considerably slow and the conversion of the substrate was less than 10% after 48 h. No reaction occurred when pyridine was used instead of Et_3N. Although there are no significant differences in selectivity between heterogeneous and homogeneous catalysts, the results of this system show the different selectivity of the products from that using Fe- and Mn-porphyrin, Cu-R_3N, and CrO_3 catalysts.[12] The kind of products formed were not influenced by the bpy ligand but intrinsically affected with Et_3N. In the absence of Et_3N the oxidation of **1c** with Ru(II)-bpy-mont catalyst gave 2-*tert*-butyldioxy-1-hydrodioxy-1,1-diphenylethane(**5c**) in 46% yield as a major product (entry 7), while with $RuCl_2(bpy)(CO)_2$ and $RuCl_2(bpy)_2{\cdot}2H_2O$ only a small amount of **5c** (8% yield) was produced in each case (entries 8 and 9). Interestingly, the Ru(II)-bpy-mont-catalyzed oxidation of **1c** under O_2 without Et_3N gave **5c** almost exclusively in 79% yield (entry 10).[13] In the case of **1b** a similar reaction occurred to give **5b** in 70% yield (entry 11). The Ru(II)-bpy-mont was easily separated after the reaction and can be provided for the second use of the oxidation of **1c**, giving **5c** in the same yield (entry 12).

Scheme 2



1a; R = H, **1b**; R = CH_3, **1c**; R = Ph

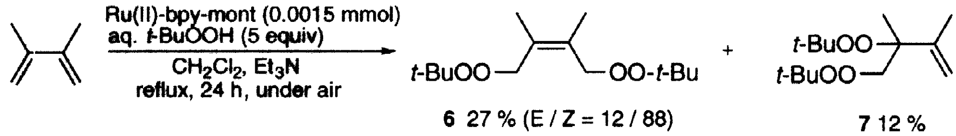
Table 1. Ru-catalyzed oxidation of aromatic alkenes with *t*-BuOOH [a]

entry	substrate	catalyst	Et_3N (mL)	products and isolated yields (%)[b]			
				2	3	4	5
1[c]	**1a**	Ru(II)-bpy-mont	0.1	30	13	–	–
2	**1b**	Ru(II)-bpy-mont	0.1	33	11	10	–
3	**1c**	Ru(II)-bpy-mont	0.1	59	19	8	tr
4	**1c**	$RuCl_2(bpy)(CO)_2$	0.1	69	19	5	tr
5	**1c**	$RuCl_2(bpy)_2{\cdot}2H_2O$	0.1	71	11	5	tr
6	**1c**	$[RuCl_2(CO)_2]_n$	0.1	63	24	5	2
7	**1c**	Ru(II)-bpy-mont	–	10	12	tr	46
8	**1c**	$RuCl_2(bpy)(CO)_2$	–	10	22	4	8
9[d]	**1c**	$RuCl_2(bpy)_2{\cdot}2H_2O$	–	27	42	tr	8
10[d]	**1c**	Ru(II)-bpy-mont	–	tr	–	18	79
11[d]	**1b**	Ru(II)-bpy-mont	–	tr	tr	1	70
12[d]	**1c**	Ru(II)-bpy-mont[e]	–	4	tr	14	79

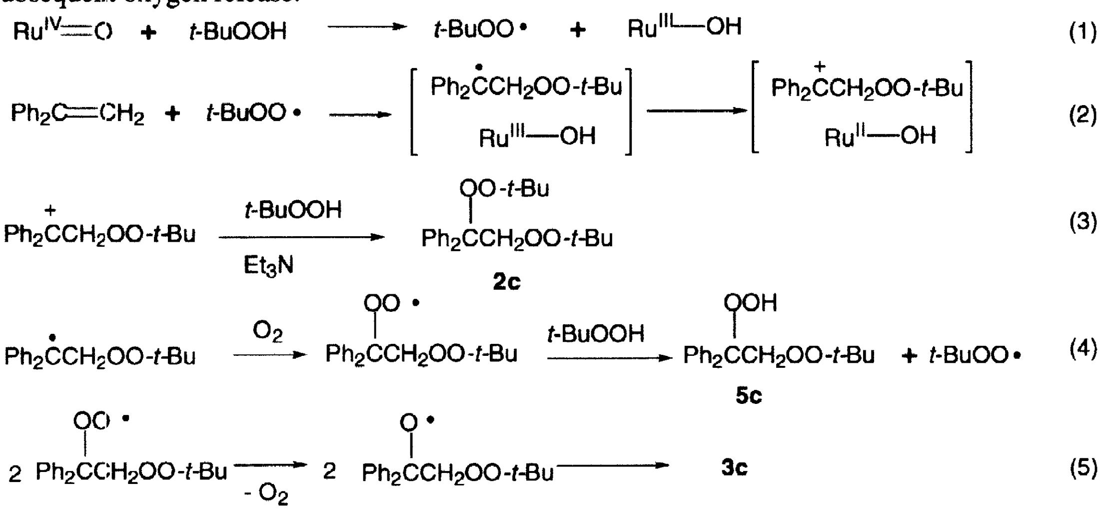
[a] Reaction condition: substrate (3 mmol), Ru(II) cat. (0.0015 mmol), 70 % aq. *t*-BuOOH (15 mmol), Et_3N (0.1 mL) in CH_2Cl_2 (5 mL) at 25 °C for 48 h under air. [b] Based on **1**. [c] Benzoic acid was also obtained in 9 % yield. [d] Reaction was performed under O_2. [e] 2nd use.

A similar oxidation of 2,3-dimethyl-1,3-butadiene occurred to give a mixture of 1,4-bis(*tert*-butyldioxy)-2,3-dimethyl-2-butene (**6**, 27% ; *E/Z* = 12/88) and 1,2-bis(*tert*-butyldioxy)-2,3-dimethyl-3-butene (**7**, 12%) (Scheme 3).

Scheme 3



The oxidation might proceed via a similar mechanism of Kharasch oxidation.[14] The oxo ruthenium(IV) as an active species might be generated as reported in the oxidation of amines[15] and *para*-substituted phenols.[16] The species Ru(IV)=O generated from Ru(II) and *t*-BuOOH abstracts hydrogen from *t*-BuOOH to give *t*-BuOO· (eq 1). The addition of *t*-BuOO· to a substrate gives a stable benzyl radical and the subsequent electron transfer leads to a benzyl cation (eq 2). Nucleophilic attack of *t*-BuOOH to the cation gives the product **2c** (eq 3). The role of Et_3N may be to accelerate the generation of active species Ru(IV)=O and to enhance the nucleophilicity of *t*-BuOOH to the cation. The result of the reaction of the conjugated diene also supports these reaction pathways including stable carbocations. On the other hand, in the absence of Et_3N, an intermediate benzyl radical reacts with O_2 to give a peroxyl radical and the subsequent hydrogen abstraction from *t*-BuOOH results in the formation of the product **5c** (eq 4). Equation 4 implies that the radical chain is constituted. In the case of the homogeneous catalyst, the intermediate peroxyl radical in high concentration undergoes self-coupling to an oxyl radical and O_2,[17] and then this oxyl radical decomposes to give benzophenone **3c** (eq 5). Although the details are not yet clear, Ru-bpy-mont system may stabilize the peroxyl radical electronically and prevent it from dimerization and subsequent oxygen release.



The system of Ru(II) and *t*-BuOOH is similar to Kharasch system, but it seems different in reactivity toward oxidation of alkenes from both Gif system and Fe- and Mn-porphyrin system.[12b] Ru(II)-bpy-mont catalyst was easily separated after reactions and this can lead to the recycle of catalyst for further reactions. Further studies on oxidation and other catalytic reactions using reusable transition metal-bpy-mont are now in progress.

References and Notes

1. a) Clark, J. H. ; In *Catalysis of Organic Reactions Using Supported Inorganic Reagents*, VCH, New York, 1994. b) Balogh, M.; Laszlo, P.; In *Organic Chemistry Using Clays*; Springer-Verlag; New York, 1993. c) Izumi, Y.; Urabe, K.; Onaka, M. In *Zeolite, Clay and Heteropoly Acids in Organic Reactions*, VCH, New York, 1992.
2. For example; a) Tateiwa, J.; Uemura, S. *J. Japan Petrol. Inst.* **1997**, 40, 329 and references therein. b) Tateiwa, J.; Kimura, A.; Takasuka, M.; Uemura, S. *J. Chem. Soc., Perkin 1*, **1997**, 2169. c) Tateiwa, J.; Hayama, E.; Nishimura, T.; Uemura, S. *J. Chem. Soc., Perkin 1*, **1997**, 1923. d) Tateiwa, J.; Horiuchi, H.; Uemura, S. *J. Chem. Soc., Perkin Trans. 2* , **1995**, 2013.
3. a) Lee, C. W.; Alper, H. *J. Org. Chem.* **1995**, *60*, 250. b) Choudary, B. M.; Koteswara Rao, K.; Pirozhkov, S. D.; Lapidus, A. L. *J. Mol. Catal.* **1994**, *88*, 23. c) Valli, V. L. K.; Alper, H. *J. Am. Chem. Soc.* **1993**, *115*, 3778. d) Choudary, B. M.; Rani, S. S.; Narender, N. *Catal. Lett.* **1993**, *19*, 299. e) Choudary, B. M.; Rani, S. S.; Narender, N. *Catal. Lett.* **1993**, *19*, 299. f) Subba Rao, Y. V.; Shobha Rani, S.; Choudary, B. M. *J. Mol. Catal.* **1992**, *75*, 141.
4. For recent reviews on ruthenium-catalyzed oxidation, see for example: Murahashi, S. -I. *Angew.Chem., Int. Ed. Engl.* **1995**, *34*, 2443.
5. Partly presented at the 70th Annual Meeting of the Chemical Society of Japan, March 1996, Tokyo, Abstract II p.1176.
6. Prepared from 6-bromo-2,2'-bipyridine, butyllithium and chloroethoxydimethylsilane: ^{1}H NMR(270 MHz, $CDCl_3$) δ 0.48 (s, 6H), 1.23 (t, *J* = 7.0 Hz, 3H), 3.82 (q, *J* = 7.0 Hz, 2H), 7.24 - 7.34 (m, 1H), 7.61 (td, *J* = 7.5, 1.3 Hz, 1H), 7.74 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.80 (td, *J* = 8.0, 1.9 Hz, 1H), 8.37 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.55 (td, *J* = 8.0, 1.1 Hz, 1H), 8.66 (dm, *J* = 4.7 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ -2.1, 18.5, 59.1, 120.5, 121.2, 123.5, 128.8, 134.9, 136.7, 149.0, 155.8, 156.7, 165.0; MS m / z (relative intensity) 257 (M^+, 91), 214 (100), 184 (43), 155 (12).
7. Colton, R.; Farthing, R. H. *Aust. J. Chem.* **1967**, *20*, 1283.
8. To a mixture of H-montmorillonite (5 g) and toluene (50 mL) was added dropwise 6-(ethoxydimethylsilyl)-2,2'-bipyridine (0.4 g, 4 mmol) at 110 °C, and the mixture was stirred at reflux for 48 h. The produced purple clay was filtered and washed with THF and then with ether by Soxhlet's extractor. The bpy-mont (5 g) was obtained after drying under vacuum. A mixture of bpy-mont (1.5 g), $[RuCl_2(CO)_2]_n$ (114 mg, 0.5 mmol) and 2-methoxyethanol (10 mL) was stirred at reflux for 2 h. The clay was collected with a centrifugal separator and washed with hot 2-methoxyethanol (10 mL × 10), THF (10 mL × 10) and ether (10 mL × 5), and then dried under vacuum. The basal spacing (d_{001}) of Ru(II)-bpy-mont obtained was 14.1 Å estimated by a sharp peak obtained on X-ray diffraction (XRD) analysis, showing clearly that the catalysts have an interlayer structure. The amount of Ru on Ru(II)-bpy-mont (1 g) was 0.03 mmol estimated by X-ray fluorescence (XRF) analysis. IR analysis showed the carbonyl absorption: ν (CO) 2013, 2073 cm^{-1}.
9. To a mixture of alkene (3 mmol), dichloromethane (5 mL), triethylamine (0.1 mL, 0.72 mmol) and Ru(II)-bpy-mont (50 mg, 0.0015 mmol) was added 70% aqueous *t*-BuOOH (1.93 g, 15 mmol) with one portion at 25 °C with a magnetic stirring. The mixture was then stirred at 25 °C for 48 h. A catalyst was collected by filtration and washed with ether. The solvent of the filtrate was evaporated and dried under vacuum. A yellowish oil left was subjected to column chromatography for purification [on SiO_2 with eluent: 2% ethyl acetate/hexane]. **2b:** a colorless oil; IR (neat) 2979, 2933, 2873, 1496, 1474, 1448, 1386, 1363, 1242, 1198, 1053, 1025, 872, 760, 698 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.20 (s, 9H), 1.25 (s, 9H), 1.65 (s, 3H), 4.23 (d, *J* = 9.6 Hz, 1H), 4.26 (d, *J* = 9.6 Hz, 1H), 7.22 – 7.37 (m, 3H), 7.45 – 7.49 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.9, 26.3, 26.6, 79.2, 79.5, 80.5, 82.9, 126.1, 127.1, 127.8, 143.0. Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 69.11; 9.49. **2c:** a colorless oil; IR (neat) 3061, 2978, 2931, 2888, 1495, 1448, 1386, 1363, 1258, 1243, 1197, 1066, 1029, 1004, 879, 757, 698 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.08 (s, 9H), 1.20 (s, 9H), 4.81 (s, 2H), 7.20 – 7.38 (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 26.2, 26.6, 77.6, 80.5, 85.7, 127.3, 127.5, 127.8, 142.0. Anal. Calcd for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found: C, 73.59; 8.56.
10. Haukka, M.; Kiviaho, J.; Ahlgren, M.; Pakkanen, T. A. *Organometallics* **1995**, *14*, 825.
11. Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *12*, 3334.
12. The formation of 1,2-bis(*tert*-butyldioxy)adduct was reported in Fe-porphyrin, Cu-R_3N and CrO_3-catalyzed oxidation of **1a** and **1b** with *t*-BuOOH: (a) Muzart, J.; N' Ait Ajjou, A. *New J. Chem.* **1994**, *18*, 731. (b) Minisci, F.; Fontana, F.; Araneo, S.; Recupero, F.; Banfi, S.; Quici, S. *J. Am. Chem. Soc.* **1995**, *117*, 226.
13. A mixed catalyst of H-mont and $RuCl_2(bpy)(CO)_2$ gave the lower yield of **5c** (19 %).
14. Kharasch, M. S.; Fono, A. *J. Org. Chem.* **1959**, *24*, 72.
15. Murahashi, S. -I.; Naota, T.; Yonemura, K. *J. Am. Chem. Soc.* **1988**, *110*, 8256.
16. Murahashi, S. -I.; Naota, T.; Miyaguchi, N.; Noda, S. *J. Am. Chem. Soc.* **1996**, *118*, 2509.
17. Fossey, J.; Lefort, D.; Sorba, J. In *Free radicals in Organic Chemistry*, John Willey & Sons, New York, 1995, p. 95.