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# Ruthenium-Catalyzed Oxidative Cleavage of Olefins to Aldehydes

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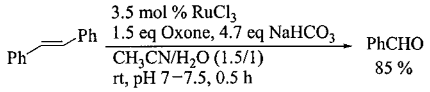
Three oxidation protocols have been developed to cleave olefins to carbonyl compounds with ruthenium trichloride as catalyst (3.5 mol %). These methods convert olefins that are not fully substituted to *aldehydes* rather than carboxylic acids. While aryl olefins were cleaved to aromatic aldehydes in excellent yields by using the system of $RuCl_3$−Oxone−$NaHCO_3$ in $CH_3CN$−$H_2O$ (1.5:1), aliphatic olefins were converted into alkyl aldehydes with $RuCl_3$−$NaIO_4$ in 1,2-dichloroethane−$H_2O$ (1:1) in good to excellent yields. It is noteworthy that terminal aliphatic olefins were cleaved to the corresponding aldehydes in excellent yields by using $RuCl_3$−$NaIO_4$ in $CH_3CN$−$H_2O$ (6:1).

## Introduction

The scission of C═C double bonds is a synthetically important reaction to degrade large compounds or to introduce oxygen functionality into molecules.[1] For the cleavage of olefins to carboxylic acids and ketones, a number of methods have been developed.[2,3] Most notably, ruthenium trichloride−sodium periodate oxidation in the $CCl_4$−$CH_3CN$−$H_2O$ (2:2:3) solvent system reported by Sharpless et al. has been widely used.[3] To obtain aldehydes from olefins that are not fully substituted, ozonization of olefins followed by a reductive workup[4] and oxidative cleavage with osmium tetraoxide−sodium periodate (Lemieux−Johnson reagent)[5] are the two most frequently employed procedures. For the sake of safety and convenience, a great deal of efforts have been directed at developing alternative methods to cleave olefins to aldehydes,[6,7] especially in a catalytic manner.[8,9] Herein, we report three new protocols for oxidative cleavage of a wide range of olefins to *aldehydes* rather than carboxylic acids with ruthenium trichloride as the catalyst.

### Scheme 1



## Results and Discussion

**Protocol I. $RuCl_3$−Oxone−$NaHCO_3$ in $CH_3CN$−$H_2O$.** The protocol exemplified in Scheme 1 involves the use of acetonitrile and water (volume ratio 1.5:1) as the homogeneous solvent system, ruthenium trichloride as the catalyst (3.5 mol %),[10] Oxone as the primary oxidant,

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[2] For ozonization followed by an oxidative workup, see: (a) Fremery, M. I.; Fields, E. K. *J. Org. Chem*. **1963**, *28*, 2537−2541. (b) Bailey, P. S. *Ind. Eng. Chem*. **1958**, *50*, 993. (c) Warnell, J. L.; Shriner, R. L. *J. Am. Chem. Soc.* **1957**, *79*, 3165−3167. For Lemieux−von Rudloff Oxidation and cation-exchange resin supported oxidation of olefins using potassium permanganate, see: (d) Lemieux, R. U.; von Rudloff, E. *Can. J. Chem*. **1955**, *33*, 1701−1709. (e) Joshi, P. L.; Hazra, B. G. *J. Chem. Res., Synop.* **2000**, 38−39. For ruthenium-based methods for oxidative cleavage of olefins to carboxylic acids, see: (f) $RuCl_3$/NaOCl: Wolfe, S.; Hasan, S. K.; Campbell, J. R. *J. Chem. Soc., Chem. Commun*. **1970**, 1420−1421. (g) $RuO_4$/$NaIO_4$ in aqueous acetone solution: Stork, G.; Meisels, A.; Davies, J. E. *J. Am. Chem. Soc.* **1963**, *85*, 3419−3425. (h) Sondheimer, F.; Mechoulam, R.; Sprecher, M. *Tetrahedron* **1964**, *20*, 2473−2485. (i) $RuO_2$/$NaIO_4$ in biphasic solvent system of $CCl_4$−$H_2O$: Torii, S.; Inokuchi, T.; Kondo, K. *J. Org. Chem*. **1985**, *50*, 4980−4982. For $CrO_3$-mediated oxidation, see: (j) Riegel, B.; Moffett, R. B.; McIntosh, A. V. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, pp 234−236. For a class of peroxotungsten complex-mediated and tungstic acid-catalyzed oxidative cleavage of olefins to carboxylic acids, see: (k) Antonelli, E.; D'Aloisio, R.; Gambaro, M.; Fiorani, T.; Venturello, C. *J. Org. Chem*. **1998**, *63*, 7190−7206. (l) Oguchi, T.; Ura, T.; Ishii, Y.; Ogawa, M. *Chem. Lett*. **1989**, 857−860.

[3] Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem*. **1981**, *46*, 3936−3938.

[4] Pappas, J. J.; Keaveney, W. P.; Gancher, E.; Berger, M. *Tetrahedron Lett*. **1966**, 4273−4278.

[5] Pappo, R.; Allen, D. S., Jr.; Lemieux, R. U.; Johnson, W. S. *J. Org. Chem*. **1956**, *21*, 478−479.

[6] (a) Berkowitz and Rylander first demonstrated that stoichiometric amount of $RuO_4$ could cleave olefins to aldehydes but poor yields of aldehydes were obtained (e.g., 10% yield of adipaldehyde from cyclohexene and 12% yield of 1-heptaldehyde from 1-octene). See: Berkowitz, L. M.; Rylander, P. N. *J. Am. Chem. Soc.* **1958**, *80*, 6682−6684. (b) Shalon and Elliott reported that one steroid olefin was successfully cleaved to the corresponding aldehyde in good yield by stoichiometric amount of ruthenium tetraoxide under neutral condition. See: Shalon, Y.; Elliott, W. H. *Synth. Commun*. **1973**, *3*, 287−291.

[7] (a) Lee et al. reported that stoichiometric amount of permanganate on moist alumina effected cleavage of olefins to aldehydes in good to excellent yield. See: Lee, D. G.; Chen, T.; Wang, Z. *J. Org. Chem*. **1993**, *58*, 2918−2919. For other permanganate-based methods for cleavage of olefins to aldehydes, see: (b) Viski, P.; Szeverényi, Z.; Simándi, L. I. *J. Org. Chem*. **1986**, *51*, 3213−3214. (c) Wiberg, K. B.; Saegebarth, K. A. *J. Am. Chem. Soc.* **1957**, *79*, 2822−2824. (d) Ogino, T.; Mochizuki, K. *Chem. Lett*. **1979**, 443. (e) Rathore, R.; Chandrasekaran, S. *J. Chem. Res., Synop*. **1986**, 458−459. For the use of stoichiometric amount of $CrO_2Cl_2$ to cleave styrene to phenylacetaldehyde and benzaldehyde, see: (f) Freeman, F.; Yamachika, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 3730−3733.

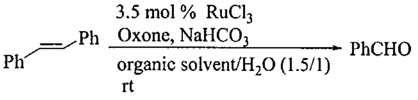
[8] For cobalt(II)-catalyzed oxidative cleavage of isoeugenol to vanillin, see: Drago, R. S.; Corden, B. B.; Barnes, C. W. *J. Am. Chem. Soc.* **1986**, *108*, 2453−2454.

[9] Recently, the use of ruthenium heteropolyanion $SiRu(H_2O)W_{11}O_{39}^{5-}$ as the catalyst enabled the cleavage of aryl olefins to aromatic aldehydes (e.g., 98% yield of benzaldehyde from the cleavage of styrene). However, under these conditions, aliphatic olefins usually gave low yields of the corresponding aldehydes. See: (a) Neumann, R.; Abu-Gnim, C. *J. Chem. Soc., Chem. Commun*. **1989**, 1324−1325. (b) Neumann, R.; Abu-Gnim, C. *J. Am. Chem. Soc.* **1990**, *112*, 6025−6031. (c) Steckhan, E.; Kandzia, C. *Synlett* **1992**, 139−140.

[10] Ruthenium(III) chloride hydrate $RuCl_3\cdot(H_2O)_n$, purchased from Acros, was utilized in the whole study. Calculations based on $n = 2$, $RuCl_3\cdot(H_2O)_2$.

10.1021/jo010122p CCC: $20.00

**Table 1. Solvent Screening Results for the Oxidative Cleavage of *trans*-Stilbene**[a]



| entry | organic solvent | time[b] (h) | yield[c] (%) |
|---|---|---|---|
| 1 | $CH_3CN$[d] | 0.5 | 85 |
| 2 | DME | 0.5 | 62 |
| 3 | THF | 1 | 65 |
| 4 | $CH_3CN/CCl_4$[e] | 1.8 | 78 |

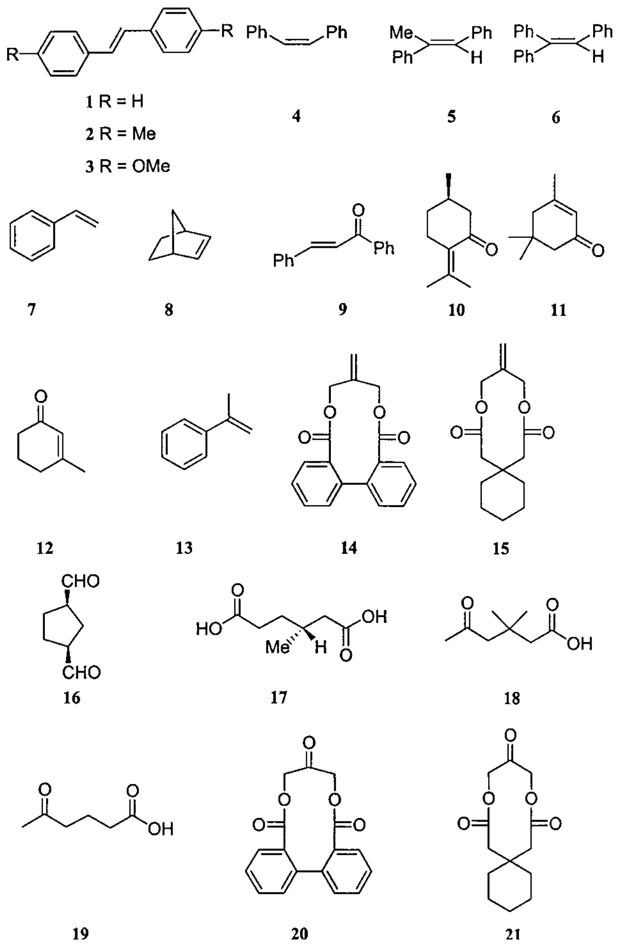
[a] Unless otherwise indicated, the reaction was carried out with 0.5 mmol of *trans*-stilbene, 0.5 mL of aqueous solution of $RuCl_3{\cdot}(H_2O)_2$ (3.5 mol %), 2 equiv of Oxone, 6.2 equiv of $NaHCO_3$, 7.5 mL of organic solvent, and 4.5 mL of water. [b] Time for complete conversion. [c] The percentage yield of benzaldehyde was calculated on the basis of the GC analysis with 1,4-dichlorobenzene as the internal standard. [d] 1.5 equiv of Oxone and 4.7 equiv of $NaHCO_3$ were employed. [e] 3.8 mL of $CH_3CN$ and 3.8 mL of $CCl_4$ were used.

and sodium bicarbonate as the buffer to maintain the neutral condition. The choice of acetonitrile as the organic solvent was based on the solvent screening results summarized in Table 1, in which *trans*-stilbene was selected as the test substrate. Among the three homogeneous solvent systems, the acetonitrile−water system gave the highest yield of benzaldehyde and required the least amount of Oxone and sodium bicarbonate (entry 1 vs entries 2 and 3). Since carbon tetrachloride is usually the essential solvent component in reactions using $RuO_4$ as the oxidant,[3,11] the heterogeneous solvent system $CCl_4$−$CH_3CN$−$H_2O$ (ratio 1:1:1.3) was also tested. Apparently, the addition of carbon tetrachloride retarded the reaction (entry 1 vs entry 4).

While $RuO_2$ (3.5 mol %) performed very well in the oxidative cleavage of *trans*-stilbene (89% yield of benzaldehyde after 20 min at room temperature), $RuCl_3$ was still the preferred ruthenium source on the basis of cost consideration. With only 1.7 mol % of $RuCl_3$, *trans*-stilbene was efficiently broken down to benzaldehyde (84% yield) in 0.8 h at room temperature. However, this low catalyst loading is not recommended for the cleavage of electron-deficient olefins such as chalcone since the conversion of chalcone was only 49% after 7 h. Thus, 3.5 mol % of $RuCl_3$ was used throughout the study.

A variety of olefins (**1**−**15**) were subjected to this new cleavage condition (Table 2). Symmetric stilbenes, trisubstituted aryl olefins, and styrene were cleanly cleaved to the corresponding aromatic aldehydes (Table 2, entries 1−7). In the case of norbornylene (**8**), the reaction was rapid to offer dialdehyde **16** in high yield (Table 2, entry 8), probably due to the release of ring strain.[12] For electron-deficient olefins such as chalcone (**9**), besides the formation of benzaldehyde, benzoic acid was obtained as the side product (Table 2, entry 9). Similar results were obtained for the other three $\alpha,\beta$-unsaturated ketones **10**−**12** (Table 2, entries 10−12).[13] The chiral center of (+)-pulegone (**10**) was not affected in the course of the reaction since the specific optical rotation of the product (i.e., diacid **17**) was identical to that reported.[14] In the case of 1,1-disubstitued olefins **13**−**15**, ketone products were obtained (Table 2, entries 13−15).[15] In particular, cyclic ketones **20** and **21**, known to be highly efficient catalysts for the in situ epoxidation of olefins by Oxone,[15b] were prepared in excellent yields after a flash cleavage

**Table 2. Oxidative Cleavage of Olefins by $RuCl_3$/Oxone Buffered with $NaHCO_3$**[a]



| entry | olefin | time (h) | product | yield (%) |
|---|---|---|---|---|
| 1 | **1** | 0.5 | PhCHO | 85 |
| 2 | **2**[b] | 0.3 | *p*-MePhCHO | 82[c] |
| 3 | **3** | 0.5 | *p*-MeOPhCHO | 66[c,d] |
| 4 | **4** | 0.4 | PhCHO | 82 |
| 5 | **5**[b] | 0.4 | PhCHO | 89 |
| | | | PhCOMe | 90[c] |
| 6 | **6**[b] | 1.1 | PhCHO | 83 |
| | | | $Ph_2CO$ | 88[c] |
| 7 | **7**[b] | 1.3 | PhCHO | 73 |
| 8 | **8** | 0.7 | **16** | 72[c] |
| 9 | **9**[b] | 2.5 | PhCHO | 70 |
| | | | $PhCO_2H$ | 68[c] |
| 10 | **10**[e] | 1.6 | **17** | 91[c,f] |
| 11 | **11**[e] | 3.4 | **18** | 94[c] |
| 12 | **12**[e] | 2.2 | **19** | 88[c] |
| 13 | **13**[b] | 1.1 | PhCOMe | 78[c] |
| 14 | **14**[g] | 0.6 | **20** | 84[c] |
| 15 | **15**[g] | 0.3 | **21** | 90[c] |

[a] Unless otherwise indicated, the reaction was carried out with 0.5 mmol of olefin, 0.5 mL of aqueous solution of $RuCl_3{\cdot}(H_2O)_2$ (3.5 mol %), 1.5 equiv of Oxone, and 4.7 equiv of $NaHCO_3$ in the solvent system of 7.5 mL of distilled $CH_3CN$ and 4.5 mL of distilled water at room temperature; 100% conversion; the percentage yield of product was obtained by GC analysis. [b] 2 equiv of Oxone and 6.2 equiv of $NaHCO_3$ were used. [c] Isolated yield. [d] Conversion of olefin **3** was 72%. [e] 2 mmol of olefin, 2.5 equiv of Oxone, and 7.8 equiv of $NaHCO_3$ were used. [f] $[\alpha]^{20}_{D} = 7.1$ (*c* 5, MeOH). [g] 0.2 mmol of olefins, 2.5 equiv of Oxone, and 7.8 equiv of $NaHCO_3$ were used.

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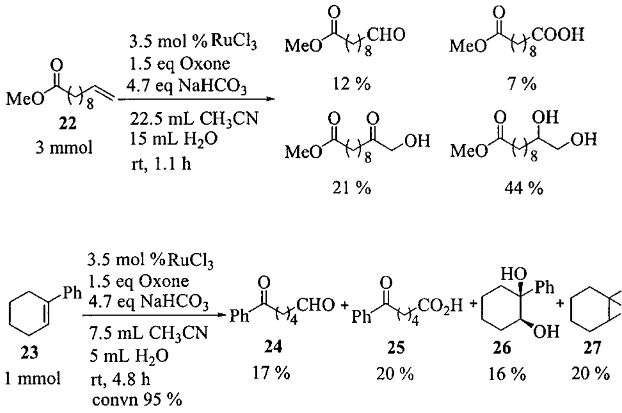
(11) Djerassi, C.; Engle, R. R. *J. Am. Chem. Soc.* **1953**, *75*, 3838−3840.

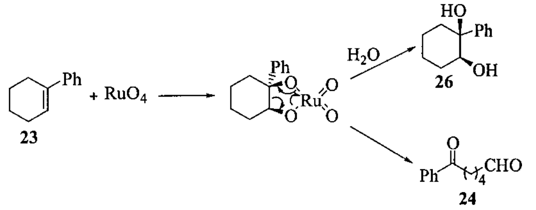
(12) Shing, T. K. M.; Tam, E. K. W.; Tai, V. W.-F.; Chung, I. H. F.; Jiang, Q. *Chem. Eur. J.* **1996**, *2*, 50−57.

(13) One paper described the oxidative cleavage of olefins **10** and **11** using the Sharpless system (ref 3), which gave the same results as ours. See: Webster, F. X.; Rivas-Enterrios, J.; Silverstein, R. M. *J. Org. Chem.* **1987**, *52*, 689−691.

## Scheme 2



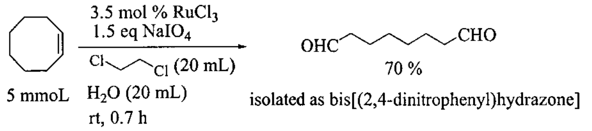
## Scheme 3



reaction. In comparison, only moderate yields (about 40%) of those two cyclic ketones were obtained after overnight cleavage using the method developed by Sharpless et al.[3]

From the cleavage results of undecylenic methyl ester (**22**) and 1-phenylcyclohexene (**23**) (Scheme 2), it was apparent that the $RuCl_3$−Oxone−$NaHCO_3$ system was not suitable for the oxidative cleavage of olefins to aliphatic aldehydes. Olefin **22**, a monosubstituted aliphatic olefin, failed to give clean aldehyde product. In the case of 1-phenylcyclohexene (**23**), a complex mixture of oxidation products were obtained. The yield of ketoacid **25** was even higher than that of keto aldehyde **24**. 1-Phenylcyclohexene oxide (**27**) was a result of the direct epoxidation mediated by Oxone.[16] However, *cis*-diol **26**[17] did not come from the hydrolysis of epoxide **27**, serving as evidence for the proposed mechanism of the cleavage reaction (Scheme 3). A cyclic ruthenium (VI) diester[18] was probably the intermediate, which yielded keto aldehyde **24** directly and *cis*-diol **26** by hydrolysis.

## Scheme 4



Since it is known that Oxone can oxidize aliphatic aldehydes to the corresponding carboxylic acids under neutral conditions,[19] sodium periodate was tested as the terminal oxidant in place of Oxone to cleave aliphatic olefins to aldehydes. We were delighted to find that $RuCl_3$−$NaIO_4$ in two different solvent systems (1,2-dichloroethane−$H_2O$ or $CH_3CN$−$H_2O$) could effectively cleave a variety of olefins to aliphatic aldehydes (*vide infra*), in sharp contrast to those ruthenium-catalyzed cleavage methods reported to yield carboxylic acids as main products.[2f−i,3]

**Protocol II. $RuCl_3$−$NaIO_4$ in 1,2-Dichloroethane−$H_2O$.** The new protocol for the cleavage of cyclooctene involved the use of sodium periodate as the terminal oxidant and two immiscible liquid phases, i.e., 1,2-dichloroethane and water, as the solvent system (Scheme 4). When the 1,2-dichloroethane layer was replaced by dichloromethane or ether, the yield of 8-oxooctanal, isolated as its bis[(2,4-dinitrophenyl)hydrazone], dropped from 70% to 58% or 40%, respectively.

The results shown in Table 3 indicated that this protocol worked well for various types of olefins. Disubstituted aliphatic olefins such as cyclohexene underwent facile cleavage to the corresponding dialdehydes in high yield (Table 3, entry 1). Trisubstituted olefin **23** was efficiently transformed to the desired keto aldehyde **24** in moderate yield (Table 3, entry 2), in contrast to the oxidation result shown in Scheme 2. (*R*)-α-Terpinyl acetate (**28**) was also smoothly converted to keto aldehyde **33**[20] in 52% yield (Table 3, entry 3), while Lemieux−Johnson reagent ($OsO_4$−$NaIO_4$) failed to cleave 1-methylcyclohexene.[5] In addition, trisubstituted acyclic olefin **29** was successfully cleaved to the desired esteraldehyde **34**[21] in excellent yield (Table 3, entry 4). Furthermore, electron-rich olefins such as glycal **30** and silyl enol ether **31** were subjected to the same cleavage conditions. While formylesteraldehyde **35**[22] was obtained from the oxidative cleavage of 3,4,6-tri-*O*-acetyl-D-glucal (**30**) in moderate yield (Table 3, entry 5), silyl enol ether **31** was converted into esteraldehyde **36** in high yield (Table 3, entry 6). Since silyl enol ethers of ketones can be easily prepared and purified,[23] this new cleavage reaction provides a mild and efficient way for the cleavage of ketones.[24] The oxidative cleavage of (+)-limonene (**32**) yielded the main product **37**,[25] together with the side product **38** (Table 3,

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[14] The specific optical rotation of (+)-3-methyladipic acid (**17**) was $[\alpha]^{20}_{D} = 7.1$ (*c* 5, MeOH). The reported value (Aldrich catalog no.: M2,738-7) was $[\alpha]^{21} = 7.2$ (*c* 5, MeOH). *The 1994−1995 Catalog Handbook of Fine Chemicals*; Aldrich Chemical Co., Inc.: Milwaukee, 1994; p 924.

[15] Under the experimental conditions of protocol I, dioxiranes could, in principle, be generated in situ from ketones and Oxone. However, no epoxidation product was detected from the cleavage reactions of **5**, **6**, and **13**−**15**. This suggested that epoxidation reactions catalyzed by ketones could not compete with the fast cleavage reactions. For examples of epoxidation reactions mediated by dioxiranes generated in situ from ketones, see: (a) Yang, D.; Wong, M.-K.; Yip, Y.-C. *J. Org. Chem.* **1995**, *60*, 3887−3889. (b) Yang, D.; Yip, Y.-C.; Tang, M.-W.; Wong, M.-K.; Cheung, K.-K. *J. Org. Chem.* **1998**, *63*, 9888−9894. (c) Yang, D.; Yip, Y.-C.; Jiao, G.-S.; Wong, M.-K. *J. Org. Chem.* **1998**, *63*, 8952−8956. (d) Denmark, S. E.; Forbes, D. C.; Hays, D. S.; DePue, J. S.; Wilde, R. G. *J. Org. Chem.* **1995**, *60*, 1391−1407.

[16] A control experiment showed that Oxone buffered with $NaHCO_3$ could even epoxidize 1-phenylcyclohexene (**23**) to the corresponding epoxide **27** in 41% yield after 4.8 h.

[17] The $^1H$ NMR and $^{13}C$ NMR data of compound **26** were identical to those reported. Kobayashi, S.; Endo, M.; Nagayama, S. *J. Am. Chem. Soc.* **1999**, *121*, 11229−11230.

[18] For the first report on the isolation of a cyclic ruthenium(VI) diester, see: Piccialli, V.; Sica, D.; Smaldone, D. *Tetrahedron Lett.* **1994**, *35*, 7093−7096.

[19] Zheng, T.-C.; Richardson, D. E. *Tetrahedron Lett.* **1995**, *36*, 833−836.

[20] A literature preparation of compound **33** involved a two-step scheme, i.e., dihydroxylation of compound **28** with potassium permanganate followed by the oxidative cleavage of the resulting diol with lead tetraacetate. See: Traber, B.; Pfander, H. *Tetrahedron* **1998**, *54*, 9011−9022.

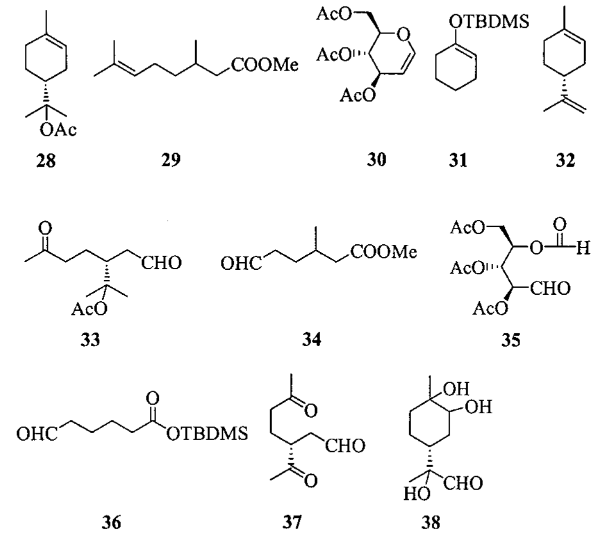
[21] CAS registry number for esteraldehyde **34** is 76712-40-8. Strobel, M. P.; Morin, L.; Paquer, D. *Fr. Nouv. J. Chim.* **1980**, *4*, 603−608.

[22] Perlin, A. S. *Can. J. Chem.* **1963**, *41*, 555−561.

[23] Mander, L. N.; Sethi, S. P. *Tetrahedron Lett.* **1984**, *25*, 5953−5956.

[24] For other methods of oxidative cleavage of silyl enol ethers, see: (a) Ozonization: Clark, R. D.; Heathcock, C. H. *J. Org. Chem.* **1976**, *41*, 1396−1403. (b) $MoO_2(acac)_2$-*t*-BuOOH: Kaneda, K.; Kii, N.; Jitsukawa, K.; Teranishi, S. *Tetrahedron Lett.* **1981**, *22*, 2595−2598.

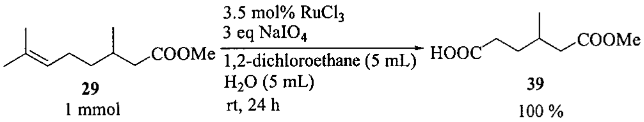
**Table 3. Oxidative Cleavage of Aliphatic Olefins by $RuCl_3/NaIO_4$ in $ClCH_2CH_2Cl/H_2O$[a]**



| entry | olefin | time (h) | product (yield, %)[b] |
|---|---|---|---|
| 1[c] | cyclohexene | 0.7 | adipaldehyde (70)[d] |
| 2[e] | **23** | 2.8 | **24** (55) |
| 3[e,f] | **28** | 1.5 | **33** (52) |
| 4 | **29** | 1.7 | **34** (80) |
| 5 | **30** | 3.5 | **35** (50) |
| 6 | **31** | 2 | **36** (75) |
| 7[e, g] | **32** | 10 | **37** (38) + **38** (10) |
| 8[h] | **1** | 1.2 | PhCHO (70) |

[a] Unless otherwise indicated, the reaction was carried out with 1 mmol of olefin, 1 mL of aqueous solution of $RuCl_3$ (3.5 mol %), 2 equiv of $NaIO_4$, 5 mL of distilled 1,2-dichloroethane, and 4 mL of distilled water at room temperature. [b] Isolated yield. [c] 5 mmol of olefin, 5 mL of an aqueous solution of $RuCl_3$ (3.5 mol %), 1.5 equiv of $NaIO_4$, 20 mL of distilled 1,2-dichloroethane, and 15 mL of distilled water at room temperature were used. [d] Isolated as bis[(2,4-dinitrophenyl)hydrazone]. [e] 5.2 mol % of $RuCl_3$ was employed to achieve a rapid reaction. [f] 70% conversion. [g] 4 equiv of $NaIO_4$ was employed. [h] 81% conversion.

**Scheme 5**

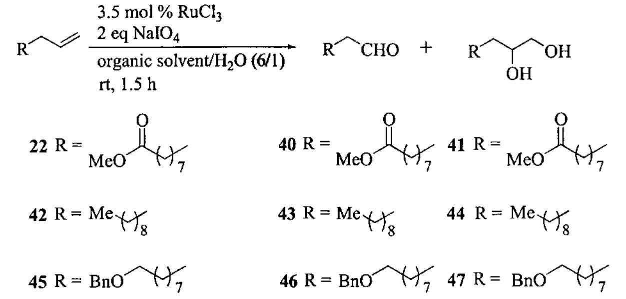


entry 7). Finally, *trans*-stilbene was cleaved to benzaldehyde in 70% yield, but apparently this reaction was quite slow compared with that under the $RuCl_3-Oxone-NaHCO_3$ system (entry 8 of Table 3 vs entry 1 of Table 2).

As shown in Scheme 5, olefin **29** was oxidized to carboxylic acid **39**[26] in quantitative yield when the amount of $NaIO_4$ was increased from 2 to 3 equiv and the reaction time was prolonged to 24 h. This indicates that the desired oxidation product, either an aldehyde or a carboxylic acid, could be obtained with $RuCl_3-NaIO_4$ in an 1,2-dichloroethane$-H_2O$ system by simple manipulation of the amount of terminal oxidant and the reaction time.

When monosubstituted aliphatic olefin **22** was subjected to the reaction conditions shown in Scheme 4, the conversion of **22** was only 38% after 2 h and the percentage yield of the desired cleavage product **40**,[27] an esteraldehyde, was 50% based on the recovered **22**. Thus, the following system of $RuCl_3-NaIO_4$ in a homogeneous solvent mixture $CH_3CN-H_2O$ was developed to cleave monosubstituted aliphatic olefins.

**Table 4. Results for Oxidative Cleavage of Monosubstituted Aliphatic Olefins[a]**



| entry | olefin | solvent system | convn (%) | yield of aldehyde[b] (%) | yield of diol[b] (%) |
|---|---|---|---|---|---|
| 1 | **22** | $CH_3CN/H_2O$ | 100 | 94 | 3 |
| 2[c] | **42** | $CH_3CN/H_2O$ | 100 | 95 | 0 |
| 3[d] | **45** | $CH_3CN/H_2O$ | 100 | 86 | 0 |
| 4[e] | **22** | $CH_3CN/H_2O$ | 79 | 71 | 1.3 |
| 5[e] | **22** | 1,4-dioxane/$H_2O$ | 75 | 64 | 8 |
| 6[e] | **22** | THF/$H_2O$ | 81 | 59 | 17 |
| 7[e] | **22** | DME/$H_2O$ | 88 | 25 | 9 |
| 8[e, f] | **22** | $CH_3CN/H_2O$ | 96 | 56 | 23 |

[a] Unless otherwise indicated, the reaction was carried out with 1 mmol of monosubstituted aliphatic olefin, 1 mL of aqueous solution of $RuCl_3{\cdot}(H_2O)_2$ (3.5 mol %), 2 mmol of $NaIO_4$, and 6 mL of organic solvent at room temperature for 1.5 h. [b] Isolated yield. [c] The reaction time was 1.6 h. [d] The reaction time was 1.1 h. [e] 1.5 equiv of $NaIO_4$ was used. [f] The volume ratio of $CH_3CN$ to $H_2O$ was 3/1, and the reaction time was 0.5 h.

**Protocol III. $RuCl_3-NaIO_4$ in $CH_3CN-H_2O$.** For monosubstituted aliphatic olefins, such as **22**, dodecene-1 (**42**), and **45**, the optimized reaction system includes the use of the homogeneous solvent system of $CH_3CN-H_2O$ (volume ratio 6:1) and 2 equiv of $NaIO_4$ (Table 4, entries 1−3). Other homogeneous solvent systems, such as 1,4-dioxane$-H_2O$, THF$-H_2O$, or DME$-H_2O$, were found to be less efficient (Table 4, entries 4−7). Increasing of the amount of $NaIO_4$ from 1.5 to 2 equiv resulted in a complete reaction and an excellent yield of aldehyde **40** (Table 4, entries 1 vs 4). The ratio of $CH_3CN$ to $H_2O$ was found to be crucial for the cleavage of **22**. When the ratio of $CH_3CN$ to $H_2O$ was 3:1, yields of aldehyde **40** and diol **41**[28] were 56% and 23%, respectively (Table 4, entry 8). However, with the increase of the $CH_3CN/H_2O$ ratio to 6:1, the isolated yield of aldehyde **40** was improved to 71% and the formation of diol **41** was suppressed to only 1.3% (Table 4, entry 4). This can be explained according to the mechanism shown in Scheme 3. The reduction of water content in the cleavage system disfavored the hydrolysis of cyclic ruthenium(VI) diester to diol.

The cleavage system developed by Sharpless et al. (i.e., $RuCl_3-NaIO_4$ in $CCl_4-CH_3CN-H_2O$) can oxidize ethers to esters.[3] However, excellent chemoselectivity was observed in the cleavage of olefin **45**[29] using our oxidation system of $RuCl_3-NaIO_4$ in $CH_3CN-H_2O$ (6/1) (Table 4, entry 3). The benzyl ether group, a commonly used

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(25) The $^1H$ NMR data of keto aldehyde **37** was identical to that reported. See: Griesbaum, K.; Hilâ, M.; Bosch, J. *Tetrahedron* **1996**, *52*, 14813−14826.

(26) The $^1H$ NMR and $^{13}C$ NMR data of **39** were identical to those reported. See: Foubelo, F.; Lloret, F.; Yus, M. *Tetrahedron* **1992**, *48*, 9531−9536.

(27) Kubo, I.; Kim, M.; Ganjian, I.; Kamikawa, T.; Yamagiwa, Y. *Tetrahedron* **1987**, *43*, 2653−2660.

(28) Hassarajani, S. A.; Subaraman, A. S.; Mamdapur, V. R. *Org. Prep. Proced. Int.* **1994**, *26*, 571−573.

hydroxyl protecting group, was kept intact over the course of the cleavage reaction.

## Conclusion

We have developed three ruthenium-based catalytic oxidation methods for cleavage of a wide range of olefins to aldehydes. As ruthenium trichloride is easy to handle and is much less expensive and toxic than $OsO_4$, these cleavage methods are expected to be useful in organic synthesis.

## Experimental Section

**General Information.** Ruthenium(III) chloride hydrate, Oxone, and sodium periodate were purchased from Acros. Commercially available olefins were purchased from Acros or Aldrich and directly used without further purification. $CH_3CN$ and 1,2-dichloroethane were distilled before use. Syntheses of substituted stilbenes **2** and **3** were carried out according to the literature procedure.[30] Preparation of cyclohexene derivative **31** was performed following the reported method.[23] Flash column chromatography was performed on E. Merck silica gel 60 (230−400 mesh ASTM) using ethyl acetate/*n*-hexane as eluting solvents. The known cleavage products were identified by comparison of the spectral and physical data with those reported. GC analysis was performed on a HP-6890 capillary gas chromatography using a flame ionization detector (FID), a 25 m × 0.32 mm × 0.52 $\mu$m HP-Ultra 1 (cross-linked methyl silicone gum) capillary column, or a 30 m × 0.32 mm × 0.5 $\mu$m HP-INNOWAX (cross-linked poly(ethylene glycol)) capillary column, with helium as the carrier gas. A stock solution of ruthenium(III) chloride was prepared by dissolving $RuCl_3 \cdot (H_2O)_2$ (842 mg, 3.5 mmol) in 100 mL of distilled water (the concentration was 0.035 M). This aqueous solution was stable for several months at room temperature.

**Typical Procedures for the Oxidative Cleavage of Olefins. Protocol I. $RuCl_3$−Oxone−$NaHCO_3$ in $CH_3CN$−$H_2O$.** To a stirred mixture of *trans*-stilbene (90 mg, 0.5 mmol) and $RuCl_3$ stock solution (0.5 mL, 0.0175 mmol, 3.5 mol % equiv) in $CH_3CN$ (7.5 mL) and distilled water (4.5 mL) was added in portions a mixture of Oxone (460 mg, 0.75 mmol) and $NaHCO_3$ (196 mg, 2.3 mmol) over a period of 10 min at room temperature. The color turned from black to yellow immediately. The reaction was monitored by TLC. After completion in 28 min, the reaction was quenched with saturated aqueous solution of $NaS_2O_3$ and then extracted with $CH_2Cl_2$ twice. The combined organic layer was washed with water and brine, respectively, dried over anhydrous $MgSO_4$, and filtered. The organic layer was subjected to GC analysis to determine the percentage yield of benzaldehyde using 1,4-dichlorobenzene as an internal standard.

**Protocol II. $RuCl_3$−$NaIO_4$ in 1,2-Dichloroethane−$H_2O$.** To a stirred mixture of compound **31** (212 mg, 1 mmol) and $RuCl_3$ stock solution (1 mL, 0.035 mmol, 3.5 mol %) in 1,2-dichloroethane (5 mL) and distilled water (4 mL) was added in portions $NaIO_4$ (428 mg, 2 mmol) over a period of 5 min at room temperature. The color turned from black to yellow immediately. The reaction was monitored by TLC. After completion in 2 h, the reaction was quenched with saturated aqueous solution of $Na_2S_2O_3$, and the two layers were separated. The aqueous layer was extracted with EtOAc three times. The combined organic layer was washed with water and brine, respectively, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography to give desired aldehyde **36** (183 mg, 75%) as a colorless oil. Analytical TLC (silica gel 60), 10% EtOAc in *n*-hexane, $R_f = 0.14$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 9.75 (t, $J$ = 1.4 Hz, 1H), 2.46 (t, $J$ = 6.7 Hz, 2H), 2.33 (t, $J$ = 6.7 Hz, 2H), 1.63 (m, 4H), 0.90 (s, 9H), 0.25 (s, 6H); $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 202.14, 173.68, 43.51, 35.59, 25.63, 25.51, 24.46, 21.44, −3.62, −4.85; IR ($CHCl_3$) 1722, 1712 cm$^{-1}$; EI-MS (20 eV) *m/z* 244 ($M^+$, 1), 243 ($M^+ - 1$, 4), 185 ($M^+ - 59$, 78), 163 (99), 75 (100); HRMS-EI *m/z* for $C_{12}H_{24}SiO_3$ ($M^+$) calcd 244.1495, found 244.1486.

**Protocol III. $RuCl_3$−$NaIO_4$ in $CH_3CN$−$H_2O$.** The procedure was identical to that of protocol II shown above, except that $CH_3CN$ was used as the organic solvent in the cleavage reactions and the ratio of $CH_3CN$ to $H_2O$ was 6:1.

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**Supporting Information Available:** $^1$H NMR and $^{13}$C NMR spectra for compounds **33**−**40**, **43**, and **46**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[29] The $^1$H NMR data of aldehyde **46** was identical to that reported. See: Naito, H.; Kawahara, E.; Maruta, K.; Maeda, M.; Sasaki, S. *J. Org. Chem.* **1995**, *60*, 4419−4427.

[30] Ogawa, K.; Sano, T.; Yoshimura, S.; Takeuchi, Y.; Toriumi, K. *J. Am. Chem. Soc.* **1992**, *114*, 1041−1051.