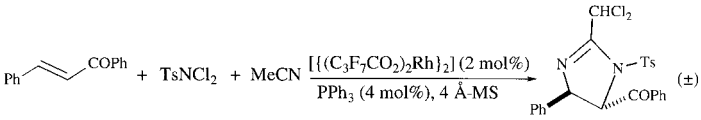
[9] a) M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett.* **1999**, *40*, 2247 – 2250; b) J. P. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674 – 2678.
[10] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953 – 956.
[11] For a recent account on the reactivity of various imidazolylidene-substituted Ru-complexes in the ring-closing olefin metathesis and enyne metathesis, see: A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* **2001**, *7*, 3236 – 3253.
[12] Alkyne **9** was prepared by alkylation of ethoxyacetylene with 5-bromo-1-pentene (*n*BuLi, THF, – 78 °C; 76 % yield).
[13] For preparation of alkynyl phosphates, see: a) P. J. Stang, *Acc. Chem. Res.* **1991**, *24*, 304 – 310; b) V. V. Zhdankin, P. J. Stang, *Tetrahedron Lett.* **1993**, *34*, 1461 – 1462.
[14] For an alternative synthesis of **22**, see: L. A. Paquette, G. J. Wells, K. A. Horn, T.-H. Yan, *Tetrahedron* **1983**, *39*, 913 – 924.
[15] DFT calculations (pBP/DN*; MacSpartan Pro 1.0.2) indicated that diene **3** was 44 kcal mol^{-1} lower in energy than the starting enyne precursor **2**.
[16] Previously, depending on the substitution pattern of the enyne precursor, either pathway I[16b,c] or pathway II[16a,d] were postulated to operate: a) A. Kinoshita, M. Mori, *Synlett* **1994**, 1020 – 1022; b) S.-H. Kim, W. J. Zuercher, N. B. Bowden, R. H. Grubbs, *J. Org. Chem.* **1996**, *61*, 1073 – 1081; c) T. R. Hoye, S. M. Donaldson, T. J. Vos, *Org. Lett.* **1999**, *1*, 277 – 279; d) T. Kitamura, Y. Sato, M. Mori, *Chem. Commun.* **2001**, 1258 – 1259.
[17] This outcome is fully consistent with prior results reported by Grubbs and co-workers: P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100 – 110.

A Novel Electrophilic Diamination Reaction of Alkenes**

Guigen Li,* Han-Xun Wei, Sun Hee Kim, and Michael D. Carducci

Electrophilic addition reactions of olefins have been of fundamental importance in organic chemistry[1] because these reactions can convert inexpensive petroleum alkenes into chemically and biologically useful compounds. At present, olefinic additions involving three or more components in a single operation are rare,[2, 3] which is probably because of the fact that only a few electrophilic addition intermediates enable multistep transformations.[4, 5] Recently, we developed several new eletrophilic addition reactions, aminohalogenation, and α,β-differentiated diamination reactions by using *N*-halogenosulfonamides as the electrophiles.[6, 7] The regio- and stereochemical features of the resulting haloamine and diamine products have unambiguously proven the formation of *N*-(*p*-tosyl),*N*-haloaziridinium or *N*-(*o*-nosyl),*N*-haloaziridinium species during the reaction processes. In our continuing research on this topic we have now discovered a novel three-component reaction (Scheme 1) which provides access to imidazolines[8] and α,β-diamino derivatives.[9, 10]



(66 %, stereoselectivity = 26 : 1
regioselectivity > 95 : 1)

Scheme 1. Chalcone-based electrophilic diamination reaction.

The current study was initiated by attempts to render the parent version of the aminohalogenation reaction asymmetric and catalytic.[6] Unfortunately, the success of this effort has been seriously limited thus far. For most of the cases we examined the reaction was either significantly deactivated or poor enantiomeric excesses resulted when chiral amine ligands were employed together with copper or zinc ions. Therefore, the search for other metal alternatives or metal – ligand complexes became necessary. When rhodium compounds were examined[11] (for example, rhodium(II) acetate dimer, rhodium(II) trifluoroacetate dimer, and rhodium(II) heptafluorobutyrate dimer) the reaction of methyl cinnamate with $TsNCl_2$ (Ts = tosyl = toluene-4-sulfonyl) led to the formation of complexes and a major side product. This side product was isolated in a yield varying between 18 – 25 % when the above catalysts were employed, although the haloamine product was generated predominantly. The subsequent X-ray structural analysis revealed that this new side product is essentially a multifuctionalized imidazoline derivative (Figure 1).

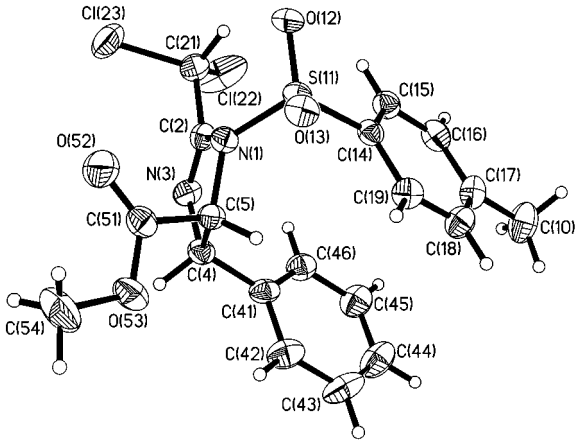


Figure 1. X-ray structure of 1-*p*-toluenesulfonyl-2-dichloromethyl-4-phenyl-5-methyloxycarbonylimidazoline.

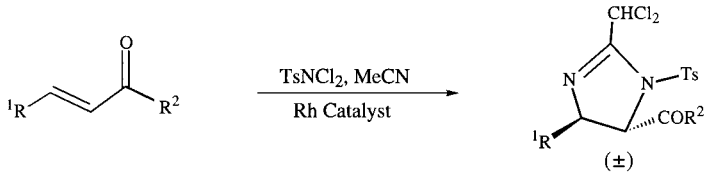
[*] Prof. Dr. G. Li, Dr. H.-X. Wei, S. H. Kim
Department of Chemistry and Biochemistry
Texas Tech University, Lubbock, TX 79409-1061 (USA)
Fax: (+1) 806) 742-1289
E-mail: qeggl@ttu.edu
Dr. M. D. Carducci[+]
Department of Chemistry
University of Arizona, Tucson, AZ 85721 (USA)
[+] To whom X-ray analysis data should be addressed.

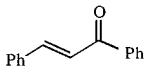
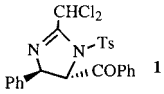
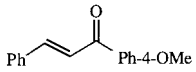
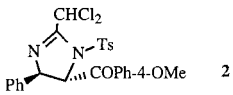
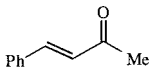
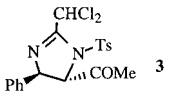
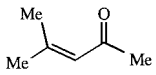
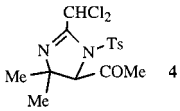
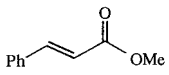
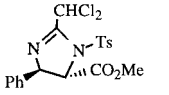
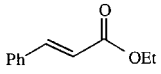
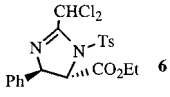
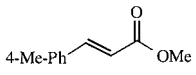
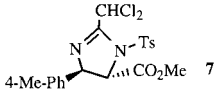
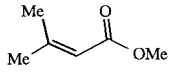
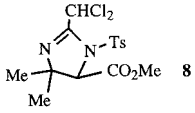
[**] We gratefully acknowledge the National Institutes of Health (GM-R15-60261), the Robert A. Welch Foundation (D-1361) for their generous support, and the National Science Foundation for their partial support of the NMR facility. We thank Mr. Subramanian Karur and Mr. Jason D. Hook for their assistance. The preliminary results of this work have been presented at the 221st ACS National Meeting, San Diego, CA, April 2001.

Encouraged by the importance of imidazolines and their imidazole derivatives, as well as diamino acids, for biomedical research,[8–10] we sought to make this side reaction the main reaciton. Of the above rhodium compounds the rhodium(II) heptafluorobutyrate dimer proved to be the catalyst which best favored formation of the imidazoline, and was thus chosen as the lead candidate for examining the effects of the reaction conditions. The model reaction was again based on the use of methyl cinnamate as the substrate (entry 5 of Table 1). Molecular sieves (4 Å) were initially found to increase the formation of imidazolines, as revealed by crude ^{1}H NMR spectroscopic analysis or thin-layer chromatography. In fact, the yield of the imidazoline product increased to nearly 35 % in the presence of 4-Å molecular sieves. Next, our attention was turned to employing ligands that would coordinate with the rhodium(II) center so as to change the catalytic reactivity of the rhodium(II) heptafluorobutyrate dimer. It was found that the Ph_3P–rhodium(II) complex generated by treating 2.0 mol % of the rhodium(II) heptafluorobutyrate dimer with 4.0 mol % of triphenylphosphane can completely inhibit the formation of haloamines. Concurrently, the yield of the imidazoline product rose to 45 %, and then to 51 % when the *N*,*N*-dichloro-*p*-toluenesulfonamide was added to the reaction system in two portions.[12]

Similar to our previous aminohalogenation systems, this reaction is also very easy to perform. Essentially, it can be conducted at room temperature in any convenient vessel of appropriate size, without the need of inert atmosphere protection. Although α,β-unsaturated esters were initially utilized and resulted in successful examples, most of these substrates did not perform as well as the α,β-unsaturated ketones in this system as shown by the low yields (45 %–51 %) realized (entries 5–7). Only in the aliphatic ester case (entry 8) was a good yield (69 %) obtained. However, the yields and selectivities were improved when α,β-unsaturated ketones were used as the substrates. Both aromatic and aliphatic ketones worked well (66–82 % for entries 1–4). Interestingly, the terminal disubstituted substrates (entries 4 and 8) resulted in the highest yields (82 and 69 %, respectively) for both ketone and ester substrate categories. No minor regioisomers were observed in the eight cases exam-

Table 1. PPh_3-[{$(C_3F_7CO_2)_2Rh$}$_2$]-catalyzed cyclic diamination.



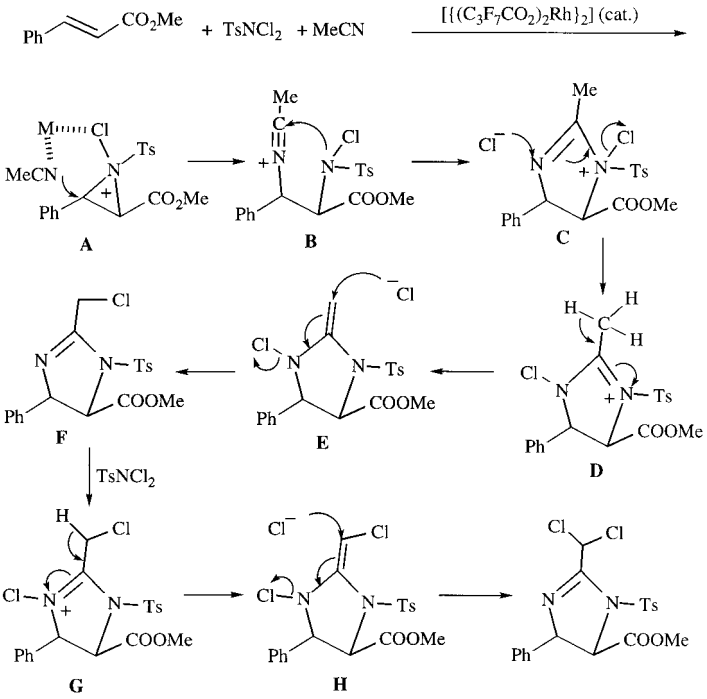
Entry	Substrates	Product (±)	m.p. [°C]	Stereoselectivty (*anti*:*syn*)[a]	yield [%][b]
1		 **1**	130–131	26:1	66
2		 **2**	58–59	40:1	68
3		 **3**	oil	50:1	66
4		 **4**	oil	–	82
5		 **5**	126–127	20:1	51
6		 **6**	102–104	25:1	49
7		 **7**	oil	25:1	45
8		 **8**	134–136	–	69

[a] Estimated by crude ^{1}H NMR determination. [b] Yields after purification by column chromatography.

  0044-8249/01/11322-4408 $ 17.50+.50/0

ined. The diastereoselectivity is good to excellent (*syn*:*anti* = 20:1 – 50:1).

Scheme 2 outlines the mechanistic proposal for the reaction. The first step is the electrophilic addition to form the *N*-(*p*-tosyl),*N*-chloroaziridinium intermediate (**A**).[13, 14] Rhodium, as well as zinc and copper, can catalyze this transformation. The Ritter-type nucleophilic attack by MeCN that

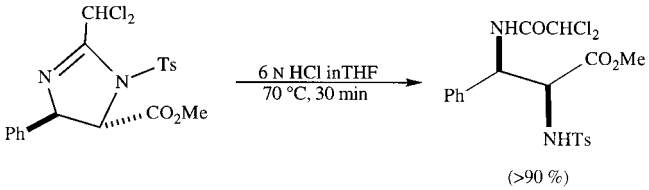


Scheme 2. Possible mechanism of diamination.

effects ring opening gives nitrilium intermediate (**B**). Since the *anti* configuration of methyl cinnamate is retained in the product, the opening of the aziridinium ring by acetonitrile clearly proceeds in a *syn* manner. It seems that the coordination of MeCN to the rhodium center occurs prior to the aziridinium ring opening. The Lewis basic moieties used in this coordination could be either the *N*-chlorine atom or the sulfonyl oxygen atom of the Ts group. The cyclization of intermediate **B** gives rise to the 1*N*-(*p*-tosyl),1*N*-chloroimidazolinium **C**, which then undergoes a 1,3-displacement of the 1*N*-chlorine atom to give 1*N*-(*p*-tosyl),3*N*-chloroimidazolinium **D**. Deprotonation of the 2-methyl group of **D** gives the methylene scaffold **E**, which enables the second S_N2'-type displacement to afford **F**. Chlorination of the 3*N* site of intermediate **F**, which gives rise to **G**, is followed by the second deprotonation of the 2-methyl group to yield **H**. At the final step, the third 1,3-displacement of chlorine results in 1-*p*-toluenesulfonyl-2-dichloromethyl-4-phenyl-5-methyloxycarbonylimidazoline.

The above mechanistic hypothesis can also account for the fact that at least two equivalents of $TsNCl_2$ are needed for the complete conversion. To further confirm the nucleophilic mechanism of forming the 2-dichloromethyl group on the imidazoline ring, the reaction (entry 1 of Table 1) was carried out in carefully degassed acetonitrile in the absence of light. The reaction rate, the yield, and stereochemical outcomes are almost the same as those obtained under normal conditions. The careful analysis of the resulting products also revealed that no chlorination occurs at the 4- and/or 5-positions of the imidazoline ring, hence a possible radical pathway can be ruled out.

Our current investigation has been extended to examine the hydrolysis of 1-*p*-toluenesulfonyl-2-dichloromethyl-4-phenyl-5-methyloxycarbonylimidazoline by treating it with a 6 N HCl solution in THF to give the α,β-differentiated diamino ester *syn*-methyl N^{α}-(4-Ts),N^{β}-dichloroacetyl diaminophenylpropionate (Scheme 3). Other synthetic properties, such as the functionalization of the $CHCl_2$ group and olefination to give 4,5-multifunctionalized imidazoles, will be studied in the future.



Scheme 3. Transformation of imidazoline to α,β-differentiated diamine.

Experimental Section

Triphenylphosphane (5.60 mg, 0.021 mmol), rhodium(II) heptafluorobutyrate dimer (10.9 mg, 0.010 mmol), and freshly distilled acetonitrile (2.50 mL) were added into a dry vial. The mixture was stirred at room temperature for 40 min before 4-Å molecular sieves (200 mg, predried in the oven at 200 °C overnight) were added. The resulting mixture was stirred for 10 min and loaded with chalcone (106 mg, 0.50 mmol; entry 1 of Table 1) and the first portion of *N*,*N*-dichloro-*p*-tolunesulfonamide (60 mg, 0.25 mmol). Stirring was continued for 4 h at RT and followed by the addition of the second portion of *N*,*N*-dichloro-*p*-toluenesulfonamide (240 mg, 1.0 mmol). The resulting light yellow slurry was stirred at RT for 40 h in the capped vial without argon protection. The 4-Å molecular sieves and other solid precipitates were filtered off and washed with EtOAc (3 × 5 mL). The organic solution was directly concentrated without quenching, purified by flash chromatography (with hexane and EtOAc (v/v = 5/1) as the eluent) to give **1** (0.162 g, 66 %) as a colorless solid. m.p. 130 – 131 °C. ^{1}H NMR (300 MHZ, $CDCl_3$): δ = 7.80 – 7.74 (m, 4H), 7.64 – 7.61 (m, 1H), 7.49 – 7.44 (m, 2H), 7.32 – 7.23 (m, 6H), 6.90 (dd, J = 1.4, 8.0 Hz, 2H), 5.56 (d, J = 4.9 Hz, 1H), 5.01 (d, J = 4.9 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.3, 156.7, 145.7, 138.7, 134.4, 134.3, 133.5, 130.1, 129.0(2), 128.8, 128.7, 128.0, 126.6, 72.3, 71.9, 61.4, 21.7; HR-MS (matrix-assisted laser desorption/ionization (MALDI) FT-MS): m/z [M^++1] found: 487.0644, calcd for $C_{24}H_{20}O_3N_2SCl_2$: 487.0644.

2: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, J = 8.6 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.22 (s, 1H), 6.92 (dd, J = 2.0, 6.8 Hz, 4H), 5.53 (d, J = 5.0 Hz, 1H), 5.01 (d, J = 5.0 Hz, 1H), 3.88 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.7, 164.5, 156.7, 145.6, 138.8, 134.5, 131.2, 130.0, 129.0, 128.6, 128.0, 126.6, 126.4, 114.2, 72.6, 71.5, 61.5, 55.6, 21.7; HR-MS (MALDI-FTMS): m/z [M^++1] found: 517.0768, calcd for $C_{25}H_{22}O_4N_2SCl_2$: 517.0750.

3: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, J = 8.4 Hz, 2H), 7.32 (s, 1H), 7.18 – 7.14 (m, 3H), 7.10 – 7.08 (m, 2H), 6.69 (d, J = 8.4 Hz, 2H), 5.14 (d, J = 4.3 Hz, 1H), 4.28 (d, J = 4.3 Hz, 1H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.0, 156.8, 146.0, 139.6, 132.6, 130.3, 128.6, 127.5, 127.4, 125.6, 75.5, 71.5, 61.8, 26.6, 21.6; HR-MS (MALDI-FTMS): m/z [M^++1] found: 425.0500, calcd for $C_{19}H_{18}O_3N_2SCl_2$: 425.0488.

4: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.21 (s, 1H), 3.99 (s, 1H), 2.47 (s, 3H), 2.23 (s, 3H), 1.21 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.5, 153.5, 146.1,

133.2, 130.4, 127.6, 70.4, 61.7, 30.7, 27.8, 23.2, 21.7; HR-MS (MALDI-FTMS): m/z [M^++1] found: 337.0484, calcd for $C_{15}H_{18}O_3N_2SCl_2$: 337.0488.

5: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.69$ (d, $J = 8.4$ Hz, 2H), 7.26 – 7.18 (m, 6H), 6.88 (d, $J = 8.4$ Hz, 2H), 5.21 (d, $J = 4.4$ Hz, 1H), 4.56 (d, $J = 4.4$ Hz, 1H), 3.81 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.7$, 156.6, 145.7, 139.2, 133.8, 130.1, 128.8, 128.0, 127.7, 125.8, 72.0, 69.2, 61.4, 53.1, 21.6; HR-MS (MALDI-FTMS): m/z [M^++1] found: 441.0446, calcd for $C_{19}H_{18}O_4N_2SCl_2$: 441.0437.

6: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.70$ (d, $J = 8.4$ Hz, 2H), 7.26 – 7.19 (m, 6H), 6.90 (d, $J = 8.4$ Hz, 2H), 5.20 (d, $J = 4.3$ Hz, 1H), 4.55 (d, $J = 4.3$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 2.42 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.3$, 156.6, 145.7, 139.3, 133.9, 130.0, 128.8, 128.0, 127.7, 125.8, 72.1, 69.3, 62.3, 61.5, 21.6, 14.0; HR-MS (MALDI-FTMS): m/z [M^++1] found: 455.0587, calcd for $C_{20}H_{20}O_4N_2SCl_2$: 455.0594.

7: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.70$ (dd, $J = 1.8$, 6.6 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.18 (s, 1H), 6.90 (d, $J = 8.2$ Hz, 2H), 6.77 (d, $J = 8.0$ Hz, 2H), 5.17 (d, $J = 4.4$ Hz, 1H), 4.54 (d, $J = 4.4$ Hz, 1H), 3.79 (s, 3H), 2.43 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.8$, 156.4, 145.7, 137.9, 136.3, 133.9, 130.0, 129.4, 127.7, 125.7, 71.9, 69.2, 61.4, 53.1, 21.6, 21.1; HR-MS (MALDI-FTMS): m/z [M^++1] found: 455.0597, calcd for $C_{20}H_{20}O_4N_2SCl_2$: 455.0594.

8: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.83$ (dd, $J = 1.9$, 6.6 Hz, 2H), 7.38 (dd, $J = 1.9$, 6.6 Hz, 2H), 7.05 (s, 1H), 4.33 (s, 1H), 3.68 (s, 3H), 2.46 (s, 3H), 1.26 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.$ 5, 153.3, 145.6, 134.3, 130.0, 127.8, 70.9, 69.5, 61.4, 52.3, 29.3, 23.1, 21.7; HR-MS (MALDI-FTMS): m/z [M^++1] found: 393.0437, calcd for $C_{15}H_{18}O_4N_2SCl_2$: 393.0449.

Received: June 18, 2001 [Z17296]

[1] a) E. Block, A. L. Schwan in *Comprehensive Organic Synthesis*, *Vol. 4* (Eds.: B. M. Trost, I. Fleming, M. F. Semmelhack), Pergamon, Oxford, **1991**, pp. 329 – 362; b) L. S. Hegedus in *Comprehensive Organic Synthesis*, *Vol. 4* (Eds.: B. M. Trost, I. Fleming, M. F. Semmelhack), Pergamon, Oxford, **1991**, pp. 551 – 570.

[2] a) B. M. Trost, A. B. Pinkerton, *J. Am. Chem. Soc.* **2000**, *122*, 8081 – 8082; b) B. M. Trost, A. B. Pinkerton, *Angew. Chem.* **2000**, *112*, 368 – 370; *Angew. Chem. Int. Ed.* **2000**, *39*, 360 – 362.

[3] For leading reviews of multicomponent reaction, see a) A. Dömling, I. Ugi, *Angew. Chem.* **2000**, *112*, 3300 – 3344; *Angew. Chem. Int. Ed.* **2000**, *39*, 3169 – 3210; b) S. Kobayashi, *Chem. Soc. Rev.* **1999**, *28*, 1 – 26. For episulfonium and episelenium ions, see refs. [4] and [5].

[4] J. Winkler, M. Finck-Estes, *Tetrahedron Lett.* **1989**, *30*, 7293 – 7296.

[5] a) A. Bewick, J. M. Mellor, W. M. Owton, *J. Chem. Perkin Trans. 1* **1985**, 1039 – 1044; b) A. Bewick, D. E. Coe, G. B. Fuller, J. M. Mellor, *Tetrahedron Lett.* **1980**, *21*, 3827 – 3828.

[6] a) G. Li, H.-X. Wei, S. H. Kim, M. Neighbors, *Org. Lett.* **1999**, *1*, 395 – 397; b) G. Li, H.-X. Wei, S. H. Kim, *Org. Lett.* **2000**, *2*, 2249 – 2252.

[7] G. Li, H.-X. Wei, S. H. Kim, *Tetrahedron Lett.* **2000**, *41*, 8699 – 8701.

[8] M. R. Grimmett in *Comprehensive Heterocyclic Chemistry*, *Vol. 5* (Eds.: A. R. Katritzky, C. W. Rees), Pergamon, Oxford, **1984**, pp. 345 – 457.

[9] D. Lucet, T. Le Gall, C. Mioskowski, *Angew. Chem.* **1998**, *110*, 2724 – 2772; *Angew. Chem. Int. Ed.* **1998**, *37*, 2580 – 2627.

[10] a) E. J. Corey, D.-H. Lee, S. Sarshar, *Tetrahedron: Asymmetry* **1995**, *6*, 3 – 6; b) A. O. Chong, K. Oshima, K. B. Sharpless, *J. Am. Chem. Soc.* **1977**, *99*, 3420 – 3426; c) M. Reetz, R. Jaeger, R. Drewlies, M. M. Hübel, *Angew. Chem.* **1991**, *103*, 76 – 78; *Angew. Chem. Int. Ed.* **1991**, *30*, 103 – 105; d) T. Hayashi, E. Kishi, V. A. Soloshonok, Y. Uozumi, *Tetrahedron Lett.* **1996**, *37*, 4969 – 4972; e) M. E. Solomon, C. L. Lynch, D. H. Rich, *Tetrahedron Lett.* **1995**, *36*, 4955 – 4958.

[11] a) M. P. Doyle, *Chem. Rev.* **1986**, *86*, 919 – 939; b) M. P. Doyle, *Aldrichimica Acta.* **1996**, *29*, 3 – 11; c) H. M. L. Davies, *Aldrichimica Acta* **1997**, *30*, 107 – 114.

[12] The common quenching treatment with aqueous Na_2SO_3 for *N,N*-dichlorosulfonamide-based reactions was not used to avoid some unknown side products. The loading of triphenylphosphane and the rhodium(II) heptafluorobutyrate dimer at 4.0 and 2.0 mol%, respectively, turned out to be near the turnover point since the reaction was not further accelerated in the presence of larger amounts of the catalyst. On the other hand, both the reaction rate and yield were diminished when a reduced amount of catalyst was used. Attempts to further optimize the reaction conditions were also made by using a variety of cosolvents of MeCN with other solvents, such as $CHCl_3$, CH_2Cl_2, toluene, and THF, in different ratios, but success was limited. An excess amount of $TsNCl_2$ (2.2 equiv) proved to be necessary for the complete consumption of the olefin starting materials. With the combination of rhodium/phosphane/4-Å MS in hand, we then went back to examine the combination of triphenylphosphane with the original rhodium compounds ($[Rh(OAc)_2]_2$ and $[Rh(OOCCF_3)_2]_2$), but failed to achieve any improvements. Surprisingly, when the triphenylphosphane ligand was replaced by tributylphosphane, only a tiny amount of the expected imidazolidine product was afforded, as revealed by crude ^{1}H NMR analysis.

[13] L. I. Krimen, D. J. Cota, *Org. React.* **1969**, *17*, 213 – 325.

[14] S.-J. Chang, *Org. Process Res. Dev.* **1999**, *3*, 232 – 234.

Efficient, Catalytic, Aerobic Oxidation of Alcohols with Octahedral Molecular Sieves**

Young-Chan Son, Vinit D. Makwana, Amy R. Howell, and Steven L. Suib*

The oxidation of alcohols to carbonyl compounds is of great interest to the fine chemicals industry and academia. Recently, catalytic oxidations of alcohols in which oxygen is the secondary oxidant have been the focus in many laboratories.[1–6] Alcohol oxidations using Ru,[2] Co,[3] Cu,[4] Pd,[5] and Pt[6] metal catalysts with additives, such as potassium carbonate, sodium bicarbonate, pyridine, molecular sieves, and phenanthroline, have been reported.

Stoichiometric metal oxidants such as chromates and active manganese dioxide have also been widely used.[7] In fact, conventional active manganese oxide has been most commonly used for allylic and benzylic oxidations. The reactivity of active manganese oxide is dependent on preparation methods, compositions, and structure.[7b, 8] Complicated preparation methods are often necessary, and the use of freshly made active manganese oxide is required. Moreover, five to fifty equivalents of this reagent are required to obtain oxidation products, which results in large amounts of nonreusable, toxic waste.

The problems associated with active manganese oxides prompted us to examine octahedral molecular sieves (OMS) as potential catalysts for alcohol oxidations. OMS materials

[*] Prof. S. L. Suib
U-3060, Department of Chemistry
Department of Chemical Engineering and Institute of Materials Science
University of Connecticut, Storrs, CT 06269 (USA)
Fax: (+1) 860-486-2981
E-mail: suib@uconnvm.uconn.edu
Y.-C. Son, V. D. Makwana, Prof. A. R. Howell
U-3060, Department of Chemistry, University of Connecticut
Storrs, CT 06269-3060 (USA)

[**] We acknowledge support of the Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy. We also thank Professor Mark E. Davis, Dr. Francis Galasso, and Dr. Lixin Cao for helpful discussions.

  0044-8249/01/11322-4410 $ 17.50+.50/0