

tions. The major discrepancy between semi-empirical and ab initio calculated tensors seemed to arise from the differences in the net charge contributions. The effective term charges of hydrogen atom appeared to be transferable among the fluoromethane molecules. In the CNDO limit, the effective term charges of fluorine atom seemed also to be insensitive to the detailed molecular structure. It is hope that this is confirmed by the more extended calculations including the configuration interactions.

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## Synthesis and Dissociation Constants of Cationic Rhodium (I)-Triphenylarsine Complexes of Unsaturated Nitriles and Aldehyde

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Reactions of  $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2$  with unsaturated nitriles and aldehyde, L, produce a series of new cationic rhodium (I) complexes,  $[\text{RhL}(\text{CO})(\text{AsPh}_3)_2]\text{ClO}_4$  (L =  $\text{CH}_2 = \text{CHCN}$ ,  $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CN}$ , *trans*- $\text{CH}_3\text{CH} = \text{CHCN}$ ,  $\text{CH}_2 = \text{CHCH}_2\text{CN}$ , *trans*- $\text{C}_6\text{H}_5\text{CH} = \text{CHCN}$ , and *trans*- $\text{C}_6\text{H}_5\text{CH} = \text{CHCHD}$ ) where L are coordinated through the nitrogen and oxygen, respectively but not through the  $\pi$ -system of the olefinic group. Dissociation constants for the reaction,  $[\text{RhL}(\text{CO})(\text{AsPh}_3)_2]\text{ClO}_4 \rightleftharpoons \text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2 + \text{L}$ , have been measured to be  $1.20 \times 10^{-4}$  M (L =  $\text{CH}_2 = \text{CHCN}$ ),  $1.05 \times 10^{-4}$  M (L =  $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CN}$ ),  $3.26 \times 10^{-5}$  M (L = *trans*- $\text{CH}_3\text{CH} = \text{CHCN}$ ) and  $6.45 \times 10^{-5}$  M (L =  $\text{CH}_2 = \text{CHCH}_2\text{CN}$ ) in chlorobenzene at 25°C, and higher than those of triphenylphosphine complexes,  $[\text{RhL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$  where L are the corresponding nitriles that are coordinated through the nitrogen atom. The differences in dissociation constants seem to be predominantly due to the differences in  $\Delta H$  (not due to the differences in  $\Delta S$ ). The weaker Rh-N (unsaturated nitriles) bonding in  $\text{AsPh}_3$  complexes than in  $\text{PPh}_3$  complexes (based on  $\Delta H$  values) suggests that the unsaturated nitriles in **2**–**5** are good  $\sigma$ -donor and poor  $\pi$ -acceptor.

### Introduction

Transition metal complexes of triphenylphosphine ( $\text{PPh}_3$ ) have been much more studied in general than the triphenylarsine ( $\text{AsPh}_3$ ) complexes although  $\text{AsPh}_3$ , through coordination, would increase the basicity of the central metal more effectively than  $\text{PPh}_3$ , and consequently  $\text{AsPh}_3$  complexes would undergo oxidative addition reaction more readily than  $\text{PPh}_3$

complexes, which could be the most important step for the catalytic hydrogenation of olefins. Physical properties and catalytic activities of rhodium(I)-triphenylphosphine complexes,  $[\text{RhL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$  (L = unsaturated nitriles,<sup>1,5</sup> and aldehydes<sup>6,7</sup> coordinated through the nitrogen and oxygen atom, respectively) have been recently investigated. It would be interesting to compare the physical properties and catalytic activities of  $\text{PPh}_3$  complexes with those of  $\text{AsPh}_3$



**2-7** are four-coordinated rhodium(I) complexes in which the unsaturated nitriles and aldehyde are coordinated through the nitrogen and oxygen atom, respectively, but not through the  $\pi$ -system of the olefinic group. It is well-known that four-coordinated rhodium(I) complexes,  $\text{RhA}(\text{CO})\text{L}_2$  ( $\text{L} = \text{PPh}_3$ ,  $\text{AsPh}_3$ ;  $\text{A} =$  anionic or neutral monodentate base), show an absorption band in the region of 350-400 nm ( $\epsilon$ , 2600-4000) which shifts with respect to the ligating atom of  $\text{A}$ .<sup>3,7,9</sup> The  $\text{RhA}(\text{CO})\text{L}_2$  shows an absorption band at 365-383 nm and 350-363 nm when  $\text{A}$  are the ligands that are coordinated through the nitrogen<sup>3,5,9</sup> and oxygen atom,<sup>6,7,9</sup> respectively. Significant increases in  $\nu_{\text{C}=\text{N}}$  of the unsaturated nitriles and decrease in  $\nu_{\text{C}=\text{O}}$  of the unsaturated aldehyde upon coordination to  $\text{Rh}(\text{CO})(\text{AsPh}_3)_2$  also unambiguously suggest the nitrogen-bonded unsaturated nitriles,<sup>3,5,10,11</sup> and oxygen-bonded unsaturated aldehydes<sup>6,12</sup> in **2-7**, while the slight decreases in  $\nu_{\text{C}=\text{C}}$  of the unsaturated nitriles observed for **2-7** are not large enough to suggest a bond through the  $\pi$ -system of the olefinic group. Strong bands at 1600-1700  $\text{cm}^{-1}$  due to the carbonyl group obscure the observation of  $\nu_{\text{C}=\text{C}}$  of both free and coordinated  $\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCHO}$ . Relatively small changes in the chemical shifts of the olefinic protons of the unsaturated nitriles and aldehyde upon coordination to  $\text{Rh}(\text{CO})(\text{AsPh}_3)_2$  (Table 1) also support that the coordination does not occur through the  $\pi$ -system of the olefinic group of  $\text{L}$ .

Except for  $\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCN}$  complexes (which is not readily understood), the triphenylarsine complexes show low  $\nu_{\text{C}=\text{O}}$  (of coordinated  $\text{CO}$ ) than the triphenylphosphine complexes (Table 1), which shows that  $\text{AsPh}_3$  is more effective electron-donor than  $\text{PPh}_3$  as expected. Electronic absorption occurs at shorter wavelength for  $\text{AsPh}_3$  complexes than for  $\text{PPh}_3$  complexes, which is in agreement with the data previously reported for the related complexes.<sup>9</sup> No significant differences have been found between  $^1\text{H-NMR}$  spectral data for  $\text{AsPh}_3$  and  $\text{PPh}_3$  complexes (see Table 1).

### Dissociation Constants

The dissociation of  $\text{L}$  (unsaturated nitriles) from  $[\text{RhL}(\text{CO})(\text{AsPh}_3)_2]\text{ClO}_4$  (equation 2) would provide somewhat important information on the catalytic activities of  $[\text{RhL}(\text{CO})(\text{AsPh}_3)_2]\text{ClO}_4$  for the hydrogenation of  $\text{L}$  to the corresponding saturated nitriles, since it may not be the nitrogen-bonded  $\text{L}$  complex but the olefinic  $\pi$ -system-bonded  $\text{L}$  complex that plays an important role in the catalytic hydrogenation of  $\text{L}$  through the well-established routes for the catalytic hydrogenation of olefins. The dissociation of  $\text{L}$  from the nitrogen-bonded  $\text{L}$  complex most likely helps the formation of the olefinic  $\pi$ -system-bonded complex. Existence of the three-coordinated complex,  $[\text{Rh}(\text{CO})(\text{AsPh}_3)_2]^+$  has coordinated rhodium(I) complexes,  $[\text{RhL}(\text{CO})(\text{AsPh}_3)_2]\text{ClO}_4$  and  $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2$  are detected according to the

$$[\text{RhL}(\text{CO})(\text{AsPh}_3)_2]\text{ClO}_4 \rightleftharpoons \text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2 + \text{L} \quad (2)$$

spectral data. It has been found that the dissociation of  $\text{L}$  (unsaturated nitriles) from  $[\text{RhL}(\text{CO})(\text{AsPh}_3)_2]\text{ClO}_4$  is considerably larger than that from  $[\text{RhL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$  (see Table 2). Dissociation constants for complexes **6** and **7** could not be obtained by measuring the electronic absorption spectra in the visible region due to the strong absorption of  $\text{trans-}$

**Table 2. Dissociation Constants and Thermodynamic Parameters in Monochlorobenzene for the Reaction,  $[\text{RhL}(\text{CO})(\text{AsPh}_3)_2]\text{ClO}_4 \rightleftharpoons \text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2 + \text{L}$ . In parentheses are given the corresponding data for  $[\text{RhL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ <sup>a</sup>**

L	Dissociation		
	Constant, $\text{M}^b$	$\Delta\text{H}$ (Kcal/mole) <sup>c</sup>	$\Delta\text{S}$ (cal/mol.deg)
$\text{CH}_2=\text{CHCN}$	$1.20 \times 10^{-4}$	$8.7 \pm 1.7$	$11 \pm 6$
	$(1.78 \times 10^{-5})$	$(9.8 \pm 0.4)$	$(11 \pm 1)$
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$	$1.05 \times 10^{-4}$	$8.2 \pm 0.3$	$9 \pm 1$
	$(2.10 \times 10^{-5})$	$(10.6 \pm 0.9)$	$(14 \pm 3)$
$\text{trans-CH}_3\text{CH}=\text{CHCN}$	$3.26 \times 10^{-5}$	$9.5 \pm 0.9$	$17 \pm 4$
	$(3.41 \times 10^{-6})$	$(11.8 \pm 0.6)$	$(14 \pm 1)$
$\text{CH}_2=\text{CHCH}_2\text{CN}$	$6.45 \times 10^{-5}$	$10.2 \pm 2.0$	$12 \pm 8$
	$(4.72 \times 10^{-6})$	$(12.4 \pm 0.1)$	$(17 \pm 3)$

<sup>a</sup>From reference 3. <sup>b</sup>At 25°C. <sup>c</sup>In the region of 25-55°C.

$\text{C}_6\text{H}_5\text{CH}=\text{CHCN}$  and  $\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCHO}$  near 300 nm (see Experimental section for the details of the measurements of dissociation constants).

The differences between the dissociation constants of  $\text{CH}_2=\text{CHCN}$  complex (**2**) and of other complexes (**3-5**) can be readily understood in terms of relative strength of  $\sigma$ -basicity of the nitrogen atom of the unsaturated nitriles. The larger dissociation constant observed for  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$  complex than those for complexes of  $\text{trans-CH}_3\text{CH}=\text{CHCN}$  and  $\text{CH}_2=\text{CHCH}_2\text{CN}$  may be due to steric effect of the methyl group adjacent to the CN group. It is also noticed that the differences in dissociation constants of **2-5** are predominantly due to the differences in  $\Delta\text{H}$  but not due to the differences in  $\Delta\text{S}$  (see Table 2). Dissociation constants are larger for  $\text{AsPh}_3$  complexes than for  $\text{PPh}_3$  complexes, which also seems predominantly due to the differences in  $\Delta\text{H}$  (see Table 2). The weaker Rh-N (unsaturated nitriles) bonding in  $\text{AsPh}_3$  complexes than in  $\text{PPh}_3$  complexes (based on  $\Delta\text{H}$  values) is understood by the fact that the unsaturated nitriles in **2-5** are good  $\sigma$ -donors but not effective  $\pi$ -acceptors since the electron density on the rhodium is found to be higher for  $\text{AsPh}_3$  complexes than for  $\text{PPh}_3$  complexes (based on  $\nu_{\text{CO}}$  data in Table 1).

### Experimental

**Physical measurements.**  $^1\text{H-NMR}$ , infrared and electronic absorption spectra were measured on a Varian 60-MHz (Model EM-360A), Shimadzu IR-440 and Shimadzu UV-240 equipped with temperature controller. Conductance measurements were obtained with a Yellow Springs Instrument Model 31 Conductivity Bridge with a Beckman Pt-Electrode conductivity Cell. Elemental analyses were carried out by Spang Microanalytical Laboratory, Eagle Harbor, MI, U.S.A.

**Materials.**  $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2$  was prepared by the reaction of  $\text{RhCl}(\text{CO})(\text{AsPh}_3)_2$ <sup>13</sup> with  $\text{AgClO}_4$  in the same manner that  $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$  was prepared.<sup>8</sup>  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$ ,  $\text{CH}_2=\text{CHCH}_2\text{CN}$  and  $\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCN}$  (Fluka Chemicals) were used as purchased.  $\text{trans-CH}_3\text{CH}=\text{CHCN}$  was separated from a mixture ( $\text{cis/trans} =$

ca.1) by preparative GC using a Carbowax 20M column.  $\text{CH}_2 = \text{CHCN}$ ,  $\text{CH}_2 = \text{CHCHO}$  and *trans*- $\text{C}_6\text{H}_5\text{CH} = \text{CHCHO}$  (Aldrich Chemicals) were distilled under reduced pressure before use.

**Preparation.**<sup>14</sup> Standard vacuum line and Schlenk-type glassware were used in handling metal complexes. All complexes **2-7** are stable in the solid state in air and in solution under nitrogen at room temperature.

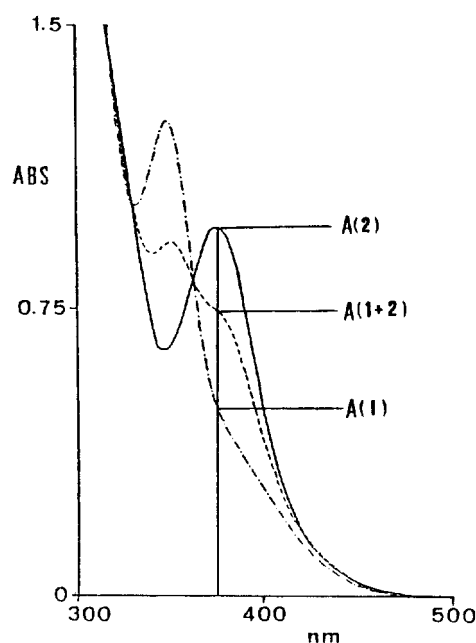
**Carbonylpropenenitrilebis(triphenylarsine)rhodium(I) perchlorate (2).** One drop (ca. 1.0 mmol) of propenenitrile was added into a benzene (40 ml) solution of  $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2$  (0.51 g, 0.6 mmol) and the solution was stirred under  $\text{N}_2$  at 25°C. Light yellow microcrystals of **2** began to precipitate within 10 minutes, collected by filtration after 30 minutes, washed with benzene (15 ml), and dried under vacuum. The yield was 0.43 g (80% based on **2**). Found: C, 52.9; H, 3.8; N, 1.7; Cl, 4.1%.  $\text{RhC}_{40}\text{H}_{33}\text{NO}_5\text{ClAs}_2$  requires C, 53.6; H, 3.7; N, 1.6; Cl, 4.0%.

**Carbonyl(2-methylpropenenitrile)bis(triphenylarsine)rhodium(I) perchlorate (3), carbonyl(trans-2-butenenitrile)bis(triphenylarsine)rhodium(I) perchlorate (4), carbonyl(3-butenitrile)bis(triphenylarsine)rhodium(I) perchlorate (5), and carbonyl(trans-3-phenyl-2-propenenitrile)bis(triphenylarsine)rhodium(I) perchlorate (6).** Were prepared in the same manner as described above for **2**, and gave satisfactory elemental analyses. Yields were 80-85%.

**Carbonyl(trans-3-phenyl-2-propenal)bis(triphenylarsine)rhodium(I) perchlorate (7).** Two drops of *trans*-3-phenyl-2-propenal (ca. 1.0 mmol) were added into a benzene (25 ml) solution of  $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2$  (0.25 g, 0.3 mmol) and the solution was stirred under  $\text{N}_2$  at 25°C. Yellow solution of the reaction mixture turned into light yellow suspension within 15 minutes, which upon cooling on ice-bath yielded light yellow microcrystals of **7** that were collected by filtration, washed with benzene (15 ml), and dried under vacuum. The yield was 0.22 g (75% based on **7**). Found: C, 56.5; H, 3.8; Cl, 3.6%.  $\text{RhC}_{46}\text{H}_{38}\text{O}_6\text{ClAs}_2$  requires C, 56.7; H, 3.9; Cl, 3.6%.

**Dissociation constants measurement.** Practically same procedures were followed to determine the dissociation constants for **2-5** at various temperatures. The experimental details for **2** are described below. Electronic spectra of **1** and **2** in the absence of  $\text{CH}_2 = \text{CHCN}$  added and **2** in the presence of excess  $\text{CH}_2 = \text{CHCN}$  were measured in monochlorobenzene to determine the absorbance, A(1) (absorbance due to **1** at 376 nm where **2** shows the absorption maximum), A(1+2) (absorbance due to **2** at 376 nm in the absence of excess  $\text{CH}_2 = \text{CHCN}$  added; A(1+2) is actually the absorbance due to **2** and **1** which is produced by the reaction,  $\mathbf{2} \rightarrow \mathbf{1} + \text{CH}_2 = \text{CHCN}$ ), and A(2) (absorbance due to **2** at 376 nm in the presence of excess  $\text{CH}_2 = \text{CHCN}$  added) (See Figure 1). Then the dissociation constant,  $K = ([\text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2][\text{CH}_2 = \text{CHCN}]) / ([\text{Rh}(\text{CH}_2 = \text{CHCN})(\text{CO})(\text{AsPh}_3)_2])$  is equal to  $(A(2) - A(1 + 2))^2 / [A(2) - A(1)](A(1 + 2) - A(1))$  where [Rh] is the total concentration of rhodium in solution.

The above-treatment for the determination of dissociation constants is also based on the following facts. (1) The  $\text{ClO}_4$  group does not dissociate from **1** in monochlorobenzene at 25-55°C, i.e., addition of  $\text{AgClO}_4$  to the solution of **1** does not show any changes in the spectrum. (2) Molar conductance of **2** in monochlorobenzene is practically zero indicating that



**Figure 1.** Electronic absorption spectra of  $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2$  (—),  $[\text{Rh}(\text{CH}_2 = \text{CHCN})(\text{CO})(\text{AsPh}_3)_2]\text{ClO}_4$  in the absence of excess  $\text{CH}_2 = \text{CHCN}$  added (---) and  $[\text{Rh}(\text{CH}_2 = \text{CHCN})(\text{CO})(\text{AsPh}_3)_2]\text{ClO}_4$  in the presence of excess  $\text{CH}_2 = \text{CHCN}$  added ( $[\text{CH}_2 = \text{CHCN}]/[\text{Rh}] = 1000$ ) (— · —) in monochlorobenzene at 25°C under nitrogen.  $[\text{Rh}] = 3.0 \times 10^{-4} \text{ M}$ . Cell pathlength = 1.0 cm. See text for A(1), A(1+2) and A(2).

the ionization,  $\mathbf{2} \rightarrow [\text{Rh}(\text{CH}_2 = \text{CHCN})(\text{CO})(\text{PPh}_3)_2]^+ + \text{ClO}_4^-$  is negligible while that of **2** in  $\text{CH}_2 = \text{CHCN}$  is  $34 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  suggesting that **2** undergoes complete ionization. Similar observation was previously reported for the conductance measurements of **1** in monochlorobenzene and in methanol.<sup>8</sup>

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the new perchlorate salts ((2)-(7)) thus far, we strongly suggest to take precaution in handling these complexes. See *J. Chem. Educ.*, **55** A 355 (1978), *Chem. Eng. News*, **61**, 4 (1983), **53**, 55 (1970), **41**, 47 (1963) and reference 8.

## 1-Methylimidazolium Chlorochromate. A New Efficient Oxidizing Agent for Oxidation of Alcohols and Oxidative Cleavage of Oximes

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1-Methylimidazolium chlorochromate was prepared by the addition of 1-methylimidazole into a solution of chromic trioxide in 6M hydrochloric acid and obtained in high yield as bright yellow crystalline solids. The reagent was found to be very effective for the oxidation of alcohols and the oxidative cleavage of oximes to the corresponding carbonyl compounds.

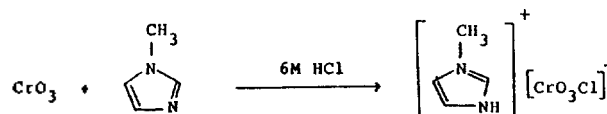
### Introduction

Since the appearance of Collins reagent in 1968,<sup>1</sup> the development of new chromium (VI) oxidizing agents for the effective and selective oxidation of organic substrates, in particular alcohols, under mild conditions has attracted a great deal of continued interest in organic synthesis. In recent years, several efficient chromium (VI) reagents such as pyridinium chlorochromate,<sup>2</sup> pyridinium dichromate,<sup>3</sup> and 2,2'-bipyridinium chlorochromate<sup>4</sup> have been introduced to improve the selectivity, the mildness and the effectiveness of the oxidant species, especially in the oxidation of complex and highly sensitive compounds. Although many chromium (VI) reagents are available for the oxidation of organic substrates,<sup>5</sup> they have certain limitations such as instability of the reagents, the need of an excess amount of the reagent, and poor selectivity to substrates. Therefore, there still exists a need for highly efficient and mild oxidizing agents. Recently, we have reported the oxidizing properties of two new chromium (VI) reagents, imidazolium dichromate<sup>6</sup> and 1,1,3,3-tetramethylguanidinium dichromate.<sup>7</sup> As part of our continuous efforts to develop new efficient oxidizing agents, we attempted to prepare imidazolium chlorochromate by the addition of imidazole into a solution of 6M hydrochloric acid and chromium trioxide at room temperature but no crystalline solids formed. Fortunately, we were able to prepare crystalline 1-methylimidazolium chlorochromate (MIC) which is expected to possess similar oxidizing properties with pyridinium chlorochromate. This article describes the preparation of 1-methylimidazolium chlorochromate and its oxidizing properties for alcohols and oximes.

### Results and Discussion

#### Preparation of 1-Methylimidazolium Chlorochromate

1-Methylimidazolium chlorochromate (MIC) was prepared by the addition of 1-methylimidazole into a solution of chromium trioxide in 6M hydrochloric acid at room temperature and obtained in 86% yield as bright yellow crystalline solids. The structure of MIC was confirmed by elemental analysis and its infrared spectrum. MIC is air stable and can be kept at room temperature for a long period of time without little decomposition.



Furthermore, MIC is very soluble in most commonly used solvents such as methylene chloride, chloroform, ether, and *N,N*-dimethylformamide, whereas it is slightly soluble in benzene and insoluble in petroleum ether.

**Oxidation of Alcohols.** Reaction of dodecanol with 1,1 equiv of the reagent in methylene chloride at room temperature gave dodecanal in an essentially quantitative yield in 12 h, indicating essentially complete utilization of the oxidant species. The reactions were complete within 6 h by the use of 1.5 equiv of the reagent under the similar conditions. Thus, remaining reaction was generally carried out with 1.1 equiv of the reagent in methylene chloride at room temperature.

Table I summarizes some experimental results obtained in this study and illustrates the efficiency, applicability and scope of this method. Under the present condition, alkyl, benzylic and allylic alcohols were cleanly oxidized to the corresponding carbonyl compounds in high yields within 24 h. It is noteworthy that the reaction can be performed on organic substrates containing acid-labile tetrahydropyranyl ether group, although it is expected that the reagent is slightly acidic. Furthermore, poor selectivities were observed in the selective oxidation of benzylic alcohols in the presence of saturated aliphatic alcohols. For instance, reaction of an 1:1 mixture of benzyl alcohol and nonyl alcohol with 1.1 equiv of the reagent in methylene chloride at room temperature in 24

†This paper is dedicated to Professor Nung Min Yoon on the occasion of his 60th birthday.