

- Wiley and Sons, 1978, P. 259.
12. Reference 11, P. 231.
 13. D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Synthesis*, **11**, 99 (1968).
 14. Although we have not experienced any incidents with

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

Sunggak Kim* and Heung Chang

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131
Received February 24, 1987

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.

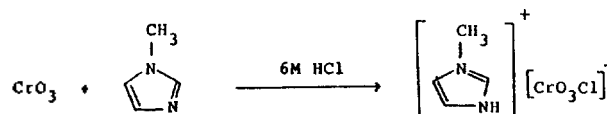
Introduction

Since the appearance of Collins reagent in 1968,¹ 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,² pyridinium dichromate,³ and 2,2'-bipyridinium chlorochromate⁴ 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,⁵ 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 dichromate⁶ and 1,1,3,3-tetramethylguanidinium dichromate.⁷ 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.

Table 1. Oxidation of Alcohols with 1-Methylimidazolium Chlorochromate^a

alcohol	time, h	isolated yield, %
	24	94
	6	89
	4 ^b	87
t-C ₆ H ₅ CH = CH-CH ₂ OH	12	82
C ₆ H ₅ CH ₂ OH	9	92
CH ₃ (CH ₂) ₁₀ CH ₂ OH	12	98
p-Cl-C ₆ H ₄ CH ₂ OH	2.5 ^b	97
(C ₆ H ₅) ₂ CHOH	24	87
C ₆ H ₅ CH(OH)CH ₂ (CH ₂) ₅ CH ₃	24	87
HO-CH ₂ C ≡ CCH ₂ O-THP	24	65
geraniol	10	90

^aThe reaction was carried out with 1.1 equiv of the reagent in methylene chloride at room temperature. ^b1.5 equiv of the reagent was used.

h gave an 80:9 mixture of benzaldehyde and nonyl aldehyde. Similar results were realized with geraniol and 1-octanol.






Oxidative Cleavage of Oximes and Hydrazones.

Oximes and hydrazones are synthetically useful functional groups and have been utilized as protective groups of the carbonyl compounds⁸ and important intermediates for alkylation of the carbonyl compounds.⁹ Thus, the cleavage of oxime and hydrazones to regenerate the carbonyl compounds is of considerable interest in organic synthesis. The recovery of the carbonyl compounds has classically involved acid hydrolysis which limits the scope of the reaction for acid-labile compounds.⁸ Thus, new mild methods for the cleavage of oximes and hydrazones have been developed. Among many methods for this purpose,¹⁰ oxidative cleavage of oximes and hydrazones with chromium (VI) reagents seems to be the method of choice,¹¹ although certain limitations have been noted. For instance, deoximation using pyridinium chlorochromate reagent requires long reaction times (12-94 h),¹² while the use of pyridinium chlorochromate and hydrogen peroxide is not suitable for regeneration of aldehydes from aldioximes.¹³

We have briefly studied the oxidative cleavage of oximes and hydrazones with 1-methylimidazolium chlorochromate. Table II shows experimental results obtained in the oxidative cleavage of oximes and hydrazones. The cleavage of benzophenone oxime with 1.2 equiv of the reagent in methylene chloride at room temperature proceeded cleanly and rapidly, yielding benzophenone in 86% yield in 1h, whereas it has been known that the reaction was not complete in 1 day using pyridinium chlorochromate.¹² Under the present conditions, p-methoxybenzaldehyde was cleanly regenerated from the corresponding oxime in 74% yield. Similarly, oximes of cyclohexanone derivatives were smoothly converted to the parent cyclohexanones in good yields.

The oxidative cleavage of N,N'-dimethylhydrazones was carried out with 1.2 equiv of reagent in methylene chloride at room temperature. N,N'-dimethylhydrazones of nonyl aldehyde and 4-t-butylcyclohexanone were cleaved to generate nonyl aldehyde and 4-t-butylcyclohexanone in 72%

Table 2. Oxidative Cleavage of Oximes with 1-Methylimidazolium Chlorochromate^a

product	time, h	isolated yield, %
	1	69
	0.5 ^b	62
	0.5 ^b	66
	0.5	64
	1	86
C ₆ H ₅ CC ₆ H ₅	0.5 ^b	88
C ₆ H ₅ CHO	0.5 ^b	50
C ₆ H ₅ COCH ₃	2.5	93
p-CH ₃ O-C ₆ H ₄ CHO	0.5	74

^aThe reaction was carried out with 1.2 equiv of the reagent in methylene chloride at room temperature. ^b1.5 equiv of the reagent was used.

and 92% yield, respectively. The cleavage of N,N'-dimethylhydrazone of 4-t-butylcyclohexanone was complete within 1 h, whereas that of N,N'-dimethylhydrazone of nonyl aldehyde required 10 h at room temperature. However, p-toluenesulfonylhydrazones of 4-t-butylcyclohexanone and nonyl aldehyde were not oxidatively cleaved with 1-methylimidazolium chlorochromate and the starting materials were recovered unchanged after prolonged stirring for 24 h at room temperature. Similarly, 2,4-dinitrophenylhydrazones were completely inert to the reagent under the similar conditions.

Experimental

¹HNMR spectra were recorded with Varian T-60A or FT-80A spectrometer and chemical shifts are expressed as δ units relative to tetramethylsilane. IR spectra were recorded on a Perkin-Elmer 267 spectrophotometer. Elemental analysis was performed by KRICT. Analytical thin layer chromatography was performed on precoated silica gel plate (0.25 mm, 60F-254, E. Merck) and silica gel (activity III, 04526, ICN) was used for column chromatography.

Alcohols employed in this study were commercially available and oximes were prepared from the corresponding carbonyl compounds by the standard procedure. All the carbonyl compounds obtained in this study are known compounds and their spectral data and physical data were identical with reported data.

Preparation of 1-Methylimidazolium Chlorochromate. To a solution of chromic trioxide (10 g, 0.1 mol) in 6M hydrochloric acid (20 ml) was slowly added 1-methylimidazole (8.2 g, 0.1 mol) with stirring and precipitated yellow-orange solids were collected on a sintered glass funnel. The product was dried in vacuo at room temperature for 1 day to give MIC (18.0 g, 86%). mp, 116-117°C; ¹HNMR (CDCl₃) δ 4.60 (s, 3H), 8.15 (s, 2H), 9.45 (s, 1H); IR (KBr) 940, 900, 760 cm⁻¹. Anal. Calcd for C₄H₇O₃N₂ClCr: C, 21.98; H, 3.23; N, 12, 82. Found: C, 22.00; H, 3.40; N, 12.80.

General Procedure for Oxidation of Alcohols. To a solution of an alcohol (2.0 mmol) in methylene chloride (5 ml)

was added MIC (2.2 mmol) and the reaction mixture was stirred at room temperature for the time given in Table I. The mixture was evaporated and ethyl ether (40 ml) was added to the residue. The supernatant was decanted from the black gum and the insoluble residue was washed three times with ethyl ether. The ether extracts were concentrated under reduced pressure and the crude product was purified by distillation.

General Procedure for Oxidative Cleavage of Oximes. To a solution of an oxime (2.0 mmol) in methylene chloride (5 ml) was added MIC (2.4 mmol). After being stirred at room temperature for the time given in Table II, the reaction mixture was evaporated and ethyl ether (40 ml) was added to the residue. The supernatant was decanted from black gum and the insoluble residue was washed three times with ethyl ether. The combined ether extracts were evaporated to dryness and the crude product was purified by distillation or by passing through a short column of silica gel.

References

1. J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).
2. E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 2647 (1975).
3. E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, 399 (1979).
4. F. S. Guziec and F. A. Luzzio, *Synthesis*, 691 (1980).
5. For recent examples, see; (a) F. S. Guziec and F. A. Luzzio, *J. Org. Chem.*, **47**, 1787 (1982); (b) X. Huang and C. Chang, *Synthesis*, 1091 (1982); (c) J. M. Aizpurua and C. Palomo, *Tetrahedron Lett.*, 4367 (1983); (d) J. M. Aizpurua, M. Juaristi, B. Lecea, and C. Palomo, *Tetrahedron*, **41**, 2903 (1985); (e) H. Firouzabadi, N. Iranpoor, F. Kiaeezadeh, and J. Toofan, *Tetrahedron*, **42**, 719 (1986).
6. S. Kim and D. C. Lhim, *Bull. Chem. Soc. Jpn.*, **59**, 3297 (1986).
7. S. Kim, D. C. Lhim, and P. H. Lee, *Bull. Korean Chem. Soc.*, **7**, 86 (1986).
8. T. W. Greene, "Protective Groups in Organic Syntheses", John Wiley & Sons, Inc., New York, 1981.
9. E. J. Corey, D. Enders, and M. G. Bock, *Tetrahedron Lett.*, 3, 7, 11 (1976).
10. (a) C. H. DePuy and B. W. Ponder, *J. Am. Chem. Soc.*, **81**, 4629 (1959); (b) S. H. Pines, J. M. Chemirda, and M. A. Kozlowski, *J. Org. Chem.*, **31**, 3446 (1966); (c) S. R. Maynez, L. Pelavin, and G. Erker, *J. Org. Chem.*, **40**, 3302 (1975); (d) E. J. Corey and S. Knapp, *Tetrahedron Lett.*, 3667 (1976); (e) D. H. R. Barton, D. J. Lester, and S. V. Ley, *Chem. Commun.*, 445 (1977); (f) G. A. Olah, J. Welch, and M. Henninger, *Synthesis*, 308 (1977); (g) E. Friedrich, W. Lutz, H. Eichenauer, and D. Ender, *Synthesis*, 893 (1977).
11. (a) E. J. Corey and J. E. Richman, *J. Am. Chem. Soc.*, **92**, 5276 (1970); (b) C. G. Rao, A. S. Radhakrishna, B. B. Singh, and S. P. Bhatnagar, *Synthesis*, 808 (1983).
12. J. R. Maloney, R. E. Lyle, and J. E. Saavedra, *Synthesis*, 212 (1978).
13. J. Drabowicz, *Synthesis*, 125 (1980).

1,4-Dicyanobutene Bridged Binuclear Iridium (I, III) Complexes and Their Catalytic Activities

Hwa-Kun Park and Chong Shik Chin*

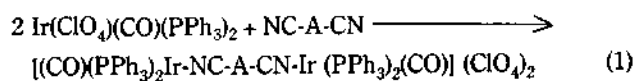
Department of Chemistry, Sogang University, Seoul 121. Received February 24, 1987

Reactions of $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ with dicyano olefins, *cis*-NCCH = CHCH₂CH₂CN (*c*DC1B), *trans*-NCCH = CHCH₂CH₂CN (*t*DC1B), *trans*-NCCH₂CH = CHCH₂CN (*t*DC2B), and NCCH₂CH₂CH₂CH₂CN (DCB) produce binuclear dicationic iridium (I) complexes, $[(\text{CO})(\text{PPh}_3)_2\text{Ir}-\text{NC}-\text{A}-\text{CN}-\text{Ir}(\text{PPh}_3)_2(\text{CO})](\text{ClO}_4)_2$ (NC-A-CN = *c*DC1B (**1a**), *t*DC1B (**1b**), *t*DC2B (**1c**), DCB (**1d**)). Complexes **1a-1d** react with hydrogen to give binuclear dicationic tetrahydrido iridium (III) complexes, $[(\text{CO})(\text{PPh}_3)_2(\text{H})_2\text{Ir}-\text{NC}-\text{A}-\text{CN}-\text{Ir}(\text{H})_2(\text{PPh}_3)_2(\text{CO})](\text{ClO}_4)_2$ (NC-A-CN = *c*DC1B (**2a**), *t*DC1B (**2b**), *t*DC2B (**2c**), DCB (**2d**)). Complexes **2a** and **2b** catalyze the hydrogenation of *c*DC1B and *t*DC1B, respectively to give DCB, while the complex **2c** is catalytically active for the isomerization of *t*DC2B to give *c*DC1B and *t*DC1B and the hydrogenation of *t*DC2B to give DCB at 100°C.

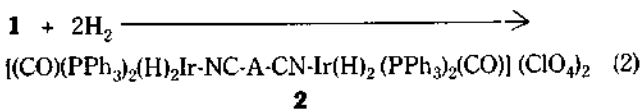
Introduction

We recently reported the synthesis and catalytic activities of monocyanoolefin complexes of rhodium(I)¹ and iridium(I, III),² $[\text{ML}(\text{CO})(\text{PPh}_3)_2] \text{ClO}_4$ (M = Rh, Ir; L = monocyanoolefins coordinated through the nitrogen atom). It would be interesting to compare these monocyanoolefin complexes with the corresponding dicyanoolefin complexes. We now wish to report the synthesis of new cationic binuclear iridium(I) and tetrahydridodiridium(III) complexes of bridging dicyanides, $[(\text{CO})(\text{PPh}_3)_2\text{Ir}-\text{NC}-\text{A}-\text{CN}-\text{Ir}(\text{PPh}_3)_2(\text{CO})](\text{ClO}_4)_2$ (**1**) and $[(\text{CO})(\text{PPh}_3)_2(\text{H})_2\text{Ir}-\text{NC}-\text{A}-\text{CN}-\text{Ir}(\text{H})_2(\text{PPh}_3)_2(\text{CO})](\text{ClO}_4)_2$ (**2**)

(CO)] $(\text{ClO}_4)_2$ (**2**) (NC-A-CN = 1,4-dicyanobutene and 1,4-dicyanobutane), and their catalytic activities for the hydrogenation and isomerization of NC-A-CN. Attempts to prepare the mononuclear complexes,



1



2