

**Acknowledgement.** This work was supported in part by the Korea Science and Engineering Foundation.

### References

1. W. B. Person and G. Zerbi, Eds., *Vibrational Intensities in Infrared and Raman Spectroscopy*, Elsevier, Amsterdam (1982).
2. K. Kim, *J. Phys. Chem.* **88**, 2394 (1984).
3. R. T. Sanderson, *Chemical Bonds and Bond Energy*, Academic, New York (1976).
4. R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, *J.*

- Chem. Phys.* **68**, 3801 (1978).
5. A. Pasternak, *Chem. Phys.* **26**, 101 (1977).
  6. R. G. Parr and R. F. Borkman, *J. Chem. Phys.* **49**, 1055 (1968).
  7. N. K. Ray, L. Samuels, and R. G. Parr, *J. Chem. Phys.* **70**, 3680 (1979).
  8. G. Herzberg, *Constants of Diatomic Molecules*, Van Nostrand, New York (1979).
  9. E. C. M. Chen, W. E. Wentworth, and J. A. Ayala, *J. Chem. Phys.* **67**, 2642 (1977).
  10. R. E. Bruns and R. E. Brown, *J. Chem. Phys.* **68**, 880 (1978).

## Reduction of Indole-2-Carboxylate and 2-Carboxamide with Magnesium in Methanol<sup>†</sup>

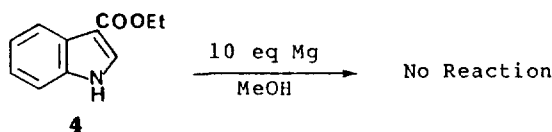
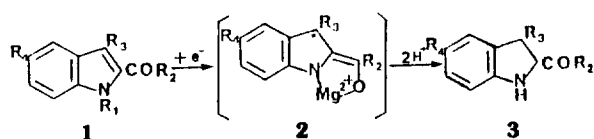
In Kwon Youn and Chwang Siek Pak\*

*Korea Research Institute of Chemical Technology P.O. Box 9, Daedeog-Danji, Chung Nam.*

Received June 1, 1987

Recently we have reported<sup>1</sup> that magnesium in methanol can be used as a mild and convenient reducing agent for the reduction of  $\alpha,\beta$ -unsaturated esters. To expand our scope for the reduction of indole derivatives<sup>2</sup> where the double bond is fused in aromatic nucleus, we have applied this reagent to various indole carboxylates (1a-e) and carboxamides (1f-g). Reduction of fused double bond of indole nuclei proceeded smoothly to give corresponding indolines in high yields as summarized in Table 1. Comparing with the known methods<sup>3</sup> for the preparation of indoline carboxylate and carboxamide, it is far more advantageous to use magnesium in methanol in its yields and reaction conditions.

As with the conjugated esters<sup>1,4</sup>, ethyl indole-2-carboxylates (1b-e) were reduced along with ester exchange by magnesium methoxide produced during the reduction to give the corresponding methyl indoline-2-carboxylates (3b-e). N-acetyl group of 1d was cleaved as expected under the reaction condition to give the same product as 1b. But the amide group of indole-2-carboxamides (1f-g) was inert to magnesium methoxide and gave the corresponding indoline-2-carboxamide (3f-g) in high yields. Interestingly 3-position substituted ethyl indole-3-carboxylate (4) was not reduced by this reagent. The starting material was completely recovered even after 10 eq. of magnesium was used.



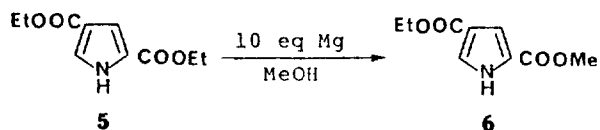
**Table 1. Reduction of 2-substituted indoles to corresponding indolines**

Entry	Starting Material(1)				Product <sup>a</sup> (3)				Mg(eq)/time(hr)	Yield <sup>b</sup> (%)
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>		
a	H	OCH <sub>3</sub>	H	H	H	OCH <sub>3</sub>	H	H	3.0/2.0	97
b	H	OC <sub>2</sub> H <sub>5</sub>	H	H	H	OCH <sub>3</sub>	H	H	2.0/2.0	96
c	H	OC <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	H	H	OCH <sub>3</sub>	CH <sub>3</sub>	H	3.5/2.0	98 <sup>c</sup>
d	COCH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	H	H	H	OCH <sub>3</sub>	H	H	3.0/1.5	90
e	H	OC <sub>2</sub> H <sub>5</sub>	H	Cl	H	OCH <sub>3</sub>	H	Cl	3.0/2.5	95 <sup>d</sup>
f	H	NH <sub>2</sub>	H	H	H	NH <sub>2</sub>	H	H	6.0/3.0	90
g	H	NHCH <sub>3</sub>	H	H	H	NHCH <sub>3</sub>	H	H	10.0/3.0	94

<sup>a</sup>all compounds have been characterized by <sup>1</sup>H NMR and mass spectroscopy. (see Note). <sup>b</sup>Yield of isolated product. <sup>c</sup>cis and trans mixture (75:25) as determined by g.l.c. and <sup>1</sup>H NMR. <sup>d</sup>Yield of crude product. Compound decomposes.

<sup>†</sup> Dedicated to Professor Nung Min Yoon on the occasion of his 60th birthday.

To check selectivity of ester exchange of 2 and 3 position, 3,5-dimethyl-2,4-dicarboethoxy pyrrole (**5**) was subjected to the same reaction conditions as the model compound. Only ester exchange occurred at 2-position to give 3,5-dimethyl-2-carbomethoxy-4-carboethoxy pyrrole (**6**) in a quantitative yield without any reduction.



Profitt and Ong reported<sup>5</sup> failure to reduce 2-phenyl indole with this reagent. Thus it is quite reasonable to assume that only the substituents at 2-position which are capable of making a proper chelate (**2**) with magnesium ion can induce reduction and ester exchange simultaneously as in the divalent ion catalysed hydrolysis of ester group.<sup>6</sup>

### Note

Physical data of products (**3a-g**) are as follow. (**3**) **a, b, d**, bp 85-86°C (0.03 torr); <sup>1</sup>H NMR (CDCl<sub>3</sub>) 3.28 (d, 2H, 7.2Hz), 3.70 (s, 3H), 4.31 (t, 1H, J = 7.2Hz), 4.70 (brs, 1H), 6.55-7.07 (m, 4H); Mass spectrum m/e (relative intensity, %) 177 (M<sup>+</sup>, 15), 118 (100), 91 (19), 89 (10) **c** Viscous oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.33 (s, 3H), 1.43 (s, 3H), 3.20-3.85 (m, 2H), 3.55 (s, 3H), 4.15 (brs, 1H), 4.20 (m, 1H), 6.35-7.00 (m, 4H); Mass spectrum m/e (relative intensity, %) 191 (M<sup>+</sup>, 12), 161 (10), 144 (68), 132 (100), 117 (32) **e** Compound decomposes

once isolated.; <sup>1</sup>H NMR was run as crude. 2.3 (d, 2H, J = 7.8Hz), 3.61 (s, 3H), 4.10 (brs, 1H), 4.30 (t, 1H, J = 7.8Hz), 6.50-7.20 (m, 3H) **f** mp 202-204°C (lit<sup>3a</sup> 208-209°C); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>+CDCl<sub>3</sub>) 2.88-3.52 (m, 2H), 4.22 (m, 1H), 4.50 (brs, 1H), 6.50-7.10 (m, 4H), 7.25 (brs, 2H); Mass spectrum m/e (relative intensity, %) 162 (M<sup>+</sup>, 11), 118 (100), 91 (20) **g** mp 111-113°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 2.82 (d, 3H, J = 5.5Hz), 2.87-3.75 (m, 2H), 4.20 (brq, 1H, J = 5.5Hz), 4.30 (m, 1H), 6.67-7.12 (m, 4H); Mass spectrum m/e (relative intensity, %) 176 (M<sup>+</sup>, 8), 118 (100), 91 (17).

### References

1. I. K. Youn, G. H. Yon, and C. S. Pak, *Tetrahedron Lett.* 1986, 2409.
2. C. W. Bird and G. W. H. Cheeseman; "Comprehensive Heterocyclic Chemistry", Pergamon Press, 1984, Vol. 4, p 255.
3. (a) C. B. Hudson, and A. V. Robertson, *Aust. J. Chem.* **20**, 1935 (1967). (b) E. J. Corey, R. J. McCaully, and H. S. Sachdev, *J. Am. Chem. Soc.* **92**, 2488 (1970). (c) Y. Omote, Y. Fujinuma, K. T. Kuo, and N. Sugiyama, *Nippon Kagaku Zasshi*, **87**, 760 (1966).
4. S. E. de Laszlo, S. V. Ley, and R. A. Porter, *J. Chem. Soc., Chem. Commun.* 1986, 344.
5. J. A. Profitt and H. H. Ong, *J. Org. Chem.*, 1979, **44**, 3972.
6. T. H. Fite and T. J. Przystas, *J. Am. Chem. Soc.*, 1985, **107**, 1041.

## Trimethylsilyl Chlorochromate. An Efficient Reagent for Oxidation of Arylmethanes to Aromatic Aldehydes

Jong Gun Lee\*, Hee Jong Lim, and Dong Soo Ha

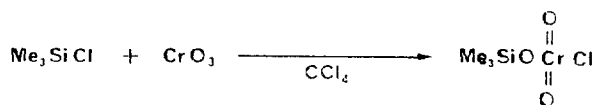
Department of Chemistry, Pusan National University, Pusan 607. Received June 8, 1987

One of the simplest way of preparing aromatic aldehydes is the direct oxidation of toluene and substituted toluenes<sup>1</sup>. The classical method of this direct oxidation is to use chromyl chloride known as Etard oxidant<sup>2</sup>. Other chromium reagents and ceric ammonium nitrate were also proved useful for this type of oxidation<sup>1,3</sup>.

As part of our effort to solubilize synthetically useful inorganic compounds and salts in organic solvents in form of (CH<sub>3</sub>)<sub>3</sub>SiX and (CH<sub>3</sub>)<sub>3</sub>Si-Y-Si(CH<sub>3</sub>)<sub>3</sub>, we investigated the oxidation properties of trimethylsilyl ester of chromic acid, chlorochromic acid and analogous chromium(VI) compounds. We now wish to report the use of trimethylsilyl chlorochromate (TSCC)<sup>4</sup> for oxidation of Arylmethanes to Aromatic Aldehydes.

This reagent was conveniently prepared by simply heating chromium trioxide and a slight excess of chlorotrimethylsilane in carbon tetrachloride and other polyhalogenated alkane solvents. Chromium trioxide completely dissolved in a

few hours to produce a homogenous solution of dark red TSCC.<sup>4</sup> Although no attempt was made to isolate or purify TSCC due to its explosive nature, it showed satisfactory NMR and mass spectral analysis<sup>5</sup>.



Chromium trioxide along with a few metallic oxides are known to be inserted into the silicon-oxygen bond of hexaalkyldisiloxanes<sup>6</sup>. However, the present insertion reaction is the rare example of such insertion into silicon-halogen bond. Sulfur trioxide is known to add into various silicon-heteroatom bonds<sup>7</sup>.

Taking into account the structural similarity of TSCC to those chromium oxidants such as pyridinium chlorochromate (PCC)<sup>8</sup> and chromyl chloride<sup>2</sup>, we expected that TSCC can be