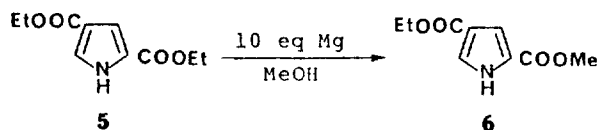To check selectivity of ester exchange of 2 and 3 position, 3,5-dimethyl-2,4-dicarboethoxy pyrrole (5) was subjected to the same reaction conditions as the model compound. Only ester exchange occurred at 2-position to give 3,5-dimethyl-2-carbomethoxy-4-carboethoxy pyrrole (6) in a quantitative yield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

Profitt and Ong reported[5] 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.[6]

Note

Physical data of products (*3a-g*) are as follow. **(3) a,b,d,** bp 85-86°C (0.03 torr); ^{1}H NMR (CDCl$_3$) 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$^+$, 15), 118 (100), 91 (19), 89 (10) **c** Viscous oil; ^{1}H NMR (CDCl$_3$) 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$^+$, 12), 161 (10), 144 (68), 132 (100), 117 (32) **e** Compound decomposes

once isolated.; ^{1}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^{3a} 208-209°C); ^{1}H NMR (DMSO-d$_6$+CDCl$_3$) 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$^+$, 11), 118 (100), 91 (20) **g** mp 111-113°C; ^{1}H NMR (CDCl$_3$) 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$^+$, 8), 118 (100), 91 (17).

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

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

As part of our effort to solubilize sythetically useful inorganic compounds and salts in organic solvents in form of (CH$_3$)$_3$ SiX and (CH$_3$)$_3$ Si-Y-Si (CH$_3$)$_3$, 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 trimethylsiyl chlorochromate (TSCC)[4] for oxidation of Arylmethanes to Aromatic Aldehydes.

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

few hours to produce a homogeous solution of dark red TSCC.[4] Although no attempt was made to isolate or purify TSCC due to it explosive nature, it showed satisfactory NMR and mass spectral analysis[5].
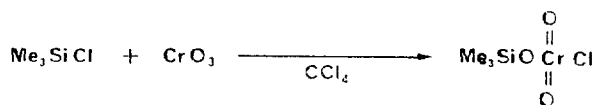
Chromium trioxide along with a few metallic oxides are known to be inserted into the silicon-oxygen bond of hexaalkyldisiloxanes[6]. However, the present insertion reaction is the rare example of such insertion into silicon-halogen bond. Sulfur trioxide is known to add into various silicon-heteroatom bonds[7].

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

Table 1. Oxidation of Arylmethanes and Related Compound with TSCC[a]

Reactant	Time(h)	Product[b]	% Yield[c]
toluene	48	benzaldehyde	78(90)
o-xylene	48	o-tolualdehyde	45(65)
p-xylene	48	p-tolualdehyde	63(73)
o-bromotoluene	45	o-bromobenzaldehyde	33(57)
p-bromotoluene	45	p-bromobenzaldehyde	44(78)
m-methoxytoluene	48	m-anisaldehyde	52
p-methoxyltoluene	48	p-anisaldehyde	60(0)
o-nitrotoluene	60	o-nitrobenzaldehyde	5(6)
p-hydroxytoluene	60	p-hydroxybenzaldehyde	5(0)
mesitylene	38	3,5-dimethylbenzaldehyde	46(6)

[a] For each H removed from the reactant, 1.8-2.0 equivalents of TSCC was used. [b] Considerable amount of hydrocarbon could be recovered. [c] Pure isolated yield. The numbers in the parenthesis refer to the yield by chromyl chloride.[9]

developed as a new selective oxidizing agent for many organic functional groups. Indeed, TSCC was found to oxidize benzyl alcohol effectively to benzaldehyde[4]. Only a trace of benzaldehyde was further oxidized to benzoic acid. Many primary and secondary alcohols were also oxidized to the corresponding carbonyl compounds in good to excellent yields.

To our surprise, TSCC was also proved effective in oxidizing toluene and substituted toluenes to the corresponding aromatic aldehydes. The procedure is very simple and straightforward.
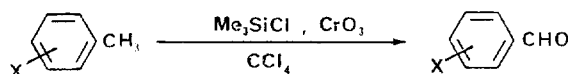
The preparation of p-anisaldehyde is representative. p-Methoxytoluene was added to the cooled carbon tetrachloride solution of 4-equivalents of TSCC prepared in situ. The reaction mixture was heated to reflux for 40-48 hours and poned into cold water. After the treatment with aqueous sodium sulfite and hydrochloric acid, the organic phase was separated and dried. The concentrated solution was chromatographed either through a silica gel column or on a tlc plate. p-Anisaldehyde was obtained in 60% yield, far better than that of Etard reaction. The yield of the other aromatic aldehydes were comparable with or better than Etard oxidation. The preparation of aldehydes in larger guantities presented no problems. The results are summarized in Table 1.

In the reaction with chromyl chloride, toluene is known to form a complex of $PhCH_3 \cdot 2CrO_2Cl_2$ type and the complex decompose to benzaldehyde when trated with water. A similar complex is believed to be formed in the oxidation with TSCC. Investigation by nmr revealed that no free aldehyde was present in the reaction mixture. The reaction could, however, be monitored by silica gel tlc. They all showed the

spots of free aldehydes. The formyl proton did not appear in the nmr until after aqueous workup or silica gel chromatography. The complex seemed to be very unstable and easily hydrolyzed by moisture adhered on silica gel. The structure of the complex and the route of its formation are believed to closely resemble those of Etard reaction[10].

Although, much work remains to be done to understand detailed aspects of the reaction, TSCC will be a valuable addition to the list of oxidizing agents for direct conversion of toluene and substitued toluenes to the corresponing aromatic aldehydes. We are currently investigating the oxidation reactions of other aromatic hydrocarbons, various type of alcohols and olefinic hydrocarbons[11] using this newly developed chromium reagent.

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