

etching can be performed regardless of the presence of light.

The removal of one atomic layer of Cd was investigated further with a measurement of surface composition. In the measurement, the x-ray photoelectron spectroscopic $3d_{5/2}$ peaks of Cd (405 eV) and Te (573 eV) were utilized. The stoichiometric surface of CdTe, prepared with the previously mentioned method and known as Cd layer is the top one, showed the I_{Te}/I_{Cd} value of 1.51 ± 0.05 . After presumable removal of one atomic layer of Cd, the ratio was change to 2.14 ± 0.12 , which indicates the amount of Te is more than that of Cd on the surface. A semiquantitative calculation⁹ was performed to evaluate the surface concentration of Te, based on an assumption that the top layer is Te (for details, see reference 10). The surface concentration of Te was turn out to be $5.09 \times 10^{-14}/\text{cm}^2$, while the theoretical one calculated from the lattice of CdTe was $4.76 \times 10^{-14}/\text{cm}^2$. The closeness of the two surface concentration values strongly implies that only one atomic layer of Cd was oxidatively stripped.

Another interesting characteristics in Figure 2 is that the potential of the charge plateau shifts in the negative direction as the illumination level increases. This observation is very important in making a pattern during atomic layer etching. For an example, at -0.2 V, removal of one atomic layer of Cd can be achieved on a surface illuminated with light of ~ 40 mW/cm², while the oxidation of Cd can not be performed on an unilluminated surface. If a light image is projected on a CdTe surface during electrochemical atomic layer etching, a negative of the projected image can be etched in a depth with an atomic resolution.

In conclusion, one atomic layer of Cd on CdTe(100) was oxidatively stripped under any illumination level. However,

the oxidation potential shifted in the cathodic direction as the illumination level increases. Such a photoelectrochemical behavior of CdTe(100) indicates that a light image projected on CdTe(100) surface can be utilized in etching out a pattern with an atomic depth resolution.

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Convenient Conversion of Carboxylic Esters to Aldehydes by Oxidation of Alkoxyaluminum Intermediate with Pyridinium Chlorochromate or Pyridinium Dichromate

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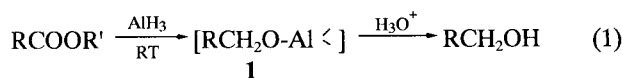
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The Oxidation of trialkyl borate¹ and trialkoxyboroxine² by pyridinium chlorochromate (PCC) affords a convenient procedure for conversion of alcohols and carboxylic acids into aldehydes. Similarly, the oxidation of alkoxyaluminum intermediate by PCC or pyridinium dichromate (PDC) provides another convenient procedure for such conversion under mild reaction conditions.³ These methods involve the reduction of alcohols and carboxylic acids with reducing agent, BH_3SMe_2 or AlH_3 , followed by oxidation of the resultant reduction products, such as alkyl borate, trialkoxyboroxine or alkoxyaluminum, with oxidizing agent. From

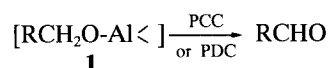
this mechanistic point of view, we decided to extend this procedure to the conversion of carboxylic esters into aldehydes. Herein we wish to introduce this new procedure which effects the transformation of carboxylic esters to aldehydes in excellent yields at room temperature.

Aluminum hydride,⁴ a very versatile reducing agent, readily reduces carboxylic esters at room temperature to form alkoxyaluminum intermediate (**I**) as an initial reduction product, which then produces the corresponding alcohols upon hydrolysis⁵ (eq 1). We believe this intermediate (without isolation) can be oxidized to aldehyde by PCC or

PDC, like the case of alcohols and carboxylic acids as reported previously.³



Indeed, the alkoxyaluminum intermediates (**1**) are readily oxidized by both PCC and PDC to the corresponding aldehydes. The procedure converts aliphatic esters to aldehydes



in 6 h at room temperature in yields of 92-98%. Actually, there is no significant difference in yields of aldehydes between PCC and PDC. A long chain ester, such as methyl laurate, undergoes the reaction to afford the aldehyde in yields of 96-98%. α,β -Unsaturated esters are also readily converted to the olefinic aldehydes. Thus, ethyl crotonate and ethyl cinnamate provide the aldehydes in yields of 95-97%. The conversion of aromatic esters by this procedure provides the corresponding aldehydes in 96-99% yields. The unsubstituted benzoates with a variety of alcohol portions are converted to benzaldehyde in yields of 98-99%, showing no difference in the yields. Alkyl-substituted benzoates, such as ethyl 3- and 4-methylbenzoates afford the corresponding aldehydes in 97-98% yields. Finally, chloro and nitro groups on the benzene ring are readily accommodated and gave aldehydes in better than 96% yield.

This reaction appears to be equally applicable to both aliphatic and aromatic carboxylic esters.⁶ The oxidizing agents are reagents of choice: the problem caused by the acidic nature of PCC can be largely eliminated by using the more neutral reagent PDC.⁷ An additional advantage is that this aldehyde synthesis can be carried out at room temperature by using very simple reagents for both reduction and oxidation reactions. Consequently, this method provides another convenient procedure, which is superior to many of the procedures previously utilized.⁸

The following procedure for the reaction of ethyl benzoate with PCC is representative. An oven-dried, 250-mL flask, fitted with a side arm and a reflux condenser connected to a mercury bubbler, was flushed with dry nitrogen and then maintained under a static pressure of nitrogen. The flask was charged with a 1.0 M solution of aluminum hydride (61 mL, 61 mmol) in THF.⁴ To the stirred solution at room temperature, ethyl benzoate (9.61 g, 61 mmol) was added dropwise and the reaction mixture was stirred for 1 h. To a well-stirred suspension of PCC (28.5 g, 132 mmol) in methylene chloride (200 mL) taken in a 500-mL flask equipped as described above, was added dropwise to the above solution of alkoxyaluminum intermediate (**1**) in THF using a cannula. The mixture was stirred for 3 h at room temperature. The small portion of this mixture was transferred to a vial and dodecane was added as an internal standard. GC using a capillary column of Carbowax 20 M indicated the presence of benzaldehyde in a yield of 99%.

The rest of the reaction mixture (60 mmol) was diluted with ethyl ether (200 mL). The supernatant liquid was filtered through Florisil® (200 g) contained in a 300-mL sintered

Table 1. Conversion of Carboxylic Esters to Aldehydes by Oxidation of Alkoxyaluminum Intermediate with Pyridinium Chlorochromate (PCC) or Pyridinium Dichromate (PDC) at Room Temperature^{a,b}

Ester	Product	Reaction time(h)	PCC	PDC
			yield (%) ^c	yield (%) ^c
Ethyl butyrate	Butyraldehyde	6	94	93
Ethyl isobutyrate	Isobutyraldehyde	6	96	92
Ethyl isovalerate	Isovaleraldehyde	6	97	95
Ethyl caproate	Hexanal	6	97(80)	92
Ethyl caprylate	Octanal	6	96	93
Methyl laurate	Dodecanal	6	98	96
Ethyl crotonate	Crotonaldehyde	3	97	96
Ethyl cinnamate	Cinnamaldehyde	3	96	95
Methyl benzoate	Benzaldehyde	3	99	98
Methyl benzoate	Benzaldehyde	3	99(82)	98(81)
Phenyl benzoate	Benzaldehyde	3	98	99
Ethyl 3-methylbenzoate	3-Methylbenzaldehyde	3	97	97
Ethyl 4-methylbenzoate	4-Methylbenzaldehyde	3	97	98
Methyl 3-methylbenzoate	3-Methylbenzaldehyde	3	97	98
Methyl 4-chlorobenzoate	4-Chlorobenzaldehyde	3	98	96
Ethyl 4-nitrobenzoate	4-Nitrobenzaldehyde	3	98	96

^aTreated with 10% excess oxidizing agent. ^bIn a THF-methylene chloride mixture solvent. ^cAnalyzed by GC. The numerals in parentheses are isolated yields.

glass funnel; the solid residue was triturated with ethyl ether (3 × 50 mL) and passed through the same Florisil column. The filtrate was concentrated and distilled under reduced pressure to give pure benzaldehyde (5.22 g, 82%); bp 62-63 °C (15 mm). The ¹H NMR spectrum agreed with that of an authentic sample.

Analogous procedure is used for the synthesis of the other aldehydes listed in Table 1. In the case of PDC as an oxidant used, actually the same procedure was adopted.

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Chlorination of Alcohols Using Potassium Chromate-based Chlorotrimethylsilane

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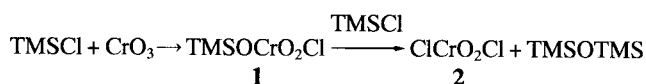
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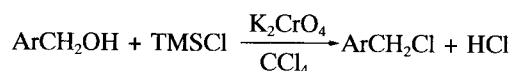
Halogenation¹ is one of the most important functional group transformations in organic chemistry. Recently, halosilanes were found to be useful for halogenation of alcohols. In general, use of chlorotrimethylsilane fails to produce alkyl chlorides. There have been only a few reports² on the use of chlorotrimethylsilane for the preparation of alkyl chlorides. Chlorotrimethylsilane^{2a} alone was known to transform some cyclopropyl alcohols into cyclopropyl chlorides, but it failed to produce chlorides from other alcohols. Potassium carbonate,³ bismuth(III) chloride,⁴ selenium dioxide,⁵ tellurium dioxide,⁶ and manganese dioxide⁷ were known to activate the chlorinating power of chlorotrimethylsilane. Chlorotrimethylsilane⁸ catalyzed by dimethyl sulfoxide was known to convert primary and tertiary alcohols to the corresponding chlorides. Bromotrimethylsilane⁹ needs a higher temperature to react with alcohols to produce alkyl bromides. Iodotrimethylsilane¹⁰ also converts alcohols to alkyl iodides under mild reaction conditions. Silicon tetrachloride¹¹ can convert alcohols to the corresponding chlorides at high temperature, although this is limited to more reactive alcohols. Potassium carbonate^{3a} and manganese dioxide⁷ were known to catalyze chlorination of alcohols using silicon tetrachloride.

In connection with the continued research for the insertion reaction of inorganic compounds to reactive silicon-halogen bond, we reported some valuable reactions for the oxidation of toluenes,¹² alcohols¹³ and olefins¹⁴ and chlorinations of alcohols.^{3a,6,7} Palomo and Aizpurua¹⁵ suggested that there would be formed an insertion product from the reaction of chromic anhydride and chlorotrimethylsilane. That is, a simple insertion of chromic anhydride into reactive silicon-chlorine bond of chlorotrimethylsilane would produce trimethylsilylchlorochromate (1)¹⁵ which Palomo *et al.* proposed as an active oxidant. There is no ground for formation of insertion product, however. We think that Palomo's hypothesis about formation of insertion product is less likely by consideration of our results.¹² We postulated that this very unstable trimethylsilylchlorochromate decomposes rapidly into chromyl chloride (2), along with the formation of hexamethyldisiloxane. Anyway, this reagent¹⁵ was proved to

be efficient for the oxidation of secondary alcohols to ketones, thiols to disulfides, and oximes to the corresponding carbonyl compounds. In the courses of exploring the broad applications of this reagent in organic synthesis, we found that the reagent also appeared to be useful for chlorinations of alcohols. In this paper, we wish to describe another convenient and interesting method which effects such chlorination of alcohols using potassium chromate and chlorotrimethylsilane.¹⁶



Some examples of results of the chlorination using chlorotrimethylsilane are summarized in Table 1. Benzyl alcohol and most of substituted benzyl alcohols such as 4-methylbenzyl alcohol, 2- and 4-methoxybenzyl alcohol, 4-chlorobenzyl alcohol, and 3-nitrobenzyl alcohol were chlorinated efficiently without competing side reactions such as oxidation. 1-Phenyl-1-propanol showed slightly different pattern. Primary alcohols containing 1-octanol and neopentyl alcohol were also chlorinated easily. Neopentyl chloride was obtained in moderate yield from the reaction of neopentyl alcohol without any skeletal rearrangement.



Most of secondary alcohols such as 2-hexanol, 4-heptanol and 2-octanol and cyclic alcohols such as cyclohexanol and menthol were also converted into the corresponding alkyl chlorides smoothly without side reactions such as skeletal migration or elimination. For example, 2-chlorooctane and menthyl chloride were obtained from 2-octanol and menthol in moderate yield. These results were different from that of reactions of thionyl chloride which is known to produce 2-chlorooctane in very low yield due to the competing elimination or migration.¹⁷ In addition to, borneol, which is very prone to skeletal migration, was found to be chlorinated