# Conversion of Alcohols to Aldehydes and Ketones by Oxidation of Trialkoxyaluminum with Pyridinium Chlorochromate

**Jin Soon Cha*, Mo-Guen Kim[1], Jong Mi Kim, Oh Oun Kwon, Joong Hyun Chun, and Sung Dong Cho[†]**

*Department of Chemistry, Yeungnam University, Kyongsan 712-749, Korea*
*[†]Department of Chemistry, Chosun University, Kwangju 501-759, Korea*
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About twenty years ago, Brown and his coworkers reported that trialkyl borates are oxidized by pyridinium chlorochromate (PCC) to aldehydes and ketones,[2] which provides another convenient procedure for the conversion of primary alcohols into the corresponding aldehydes in essentially quantitative yields. This method involves the reaction of alcohols with borane-methyl sulfide (BMS), followed by oxidation of the resultant trialkyl borate with PCC (Eq. 1).

$$3\ RCH_2OH + BH_3 \xrightarrow{RT \rightarrow 100^\circ} B(OCH_2R)_3 + 3\ H_2\ \uparrow$$

$$B(OCH_2R)_3 \xrightarrow[100^\circ,\ 1\ h]{PCC} 3\ RCHO \qquad (1)$$

However, the reaction conditions are rather drastic: heating the reaction mixture at 100 °C is desirable for both the borate formation and oxidation steps to achieve rapid conversion.

In this communication, we report an alternative method for the conversion of alcohols into the corresponding aldehydes and ketones using alane (aluminum hydride) instead of borane, which in turn provides another convenient procedure under much milder conditions. The method involves the reaction of alcohols with aluminum hydride, followed by oxidation of the resultant trialkoxyaluminum with PCC, similar to the case of the borane-involved procedure.

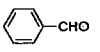
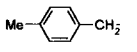
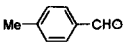
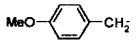
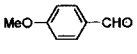
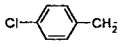
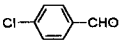
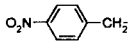
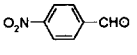
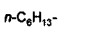
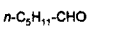
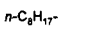
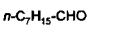
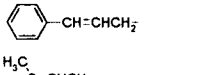
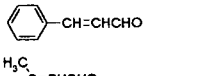
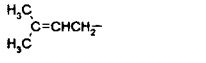
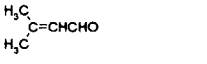
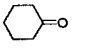
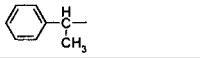
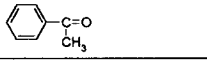
Trialkoxyaluminums are readily prepared from the reactions of alcohols with aluminum hydride[3,4] at 0 °C or room temperature (Eq. 2). A representative set of trialkoxyaluminum was prepared. The trialkoxyaluminum was oxidized with PCC in a mixed solvent of THF and methylene chloride at room temperature. The reaction is applicable to the broad range of many substituents such as chloro, methoxy, nitro and even alkene groups. The reactions were all complete in 1 or 3 h, providing essentially quantitative yields of aldehydes and ketones determined by GC analysis. The pure aldehydes and ketones were isolated by distillation after the reaction mixture being filtered through a Florisil® column.

$$3ROH + AlH_3 \xrightarrow{0^\circ \rightarrow RT} (RO)_3Al + 3\ H_2\ \uparrow \qquad (2)$$

As is the case of borates,[2] the reaction of trialkoxyaluminum with PCC does not produce water so that this procedure is free of a possible problem in the case of certain aldehydes and ketones containing groups sensitive to water. Moreover, the reactions both in the steps of trialkoxyaluminum formation and oxidation are much faster than the correponding reactions with alkyl borates, apparently due to the more reactive property of aluminum hydride and to the bigger atomic size of aluminum. The characteristic feature of this reaction arises from a direct conversion of trialkoxyaluminum as an intermediate into the carbonyl compounds. Therefore, a variety of application of this kind would be possible. These possibilities are under examination.

The following experimental procedure is illustrative. To an oven-dried, nitrogen-flushed 100-mL round-bottom flask, fitted with a septum inlet, a magnetic stirring bar, and a reflux condenser leading to a mercury bubbler, a 1.10 M solution of aluminum hydride[5] (18.2 mL, 20 mmol) in THF was injected and the solution was kept at 0 °C with the aid of an ice-water bath. The mixture was stirred at 0 °C and a 3.0 M solution of 1-octanol (20.0 mL, 60 mmol) was added dropwise with a syringe. After the addition was complete, the mixture was then allowed to room temperature and stirred for 3 h. In another oven-dried, nitrogen-flushed, 500-mL round-bottom flask, fitted with a septum inlet, a magnetic stirring bar, and a reflux condenser lead-

**Table 1.** Oxidation Trialkoxyaluminum with Pyridinium Chlorochromate (PCC) in Tetrahydrofuran and Methylene Chloride at Room Temperature[a]

| Alkyl group of $(RO)_3Al$ | Product | Yield (%)[b,c] |
|---|---|---|
|  |  | 98 |
|  |  | 97 |
|  |  | 97 |
|  |  | 98 |
|  |  | 96 |
|  |  | 96 |
|  |  | 97(78)[e] |
|  |  | 99 |
|  |  | 96 |
|  |  | 99(82)[e] |
|  |  | 98[d] |

[a] $(RO)_3Al$ : PCC = 1 : 6. [b] GC yields. [c] Reacted for 1 h at room temperature, except where indicated otherwise. [d] Reacted for 3 h at room temperature. [e] Isolated yield.

ing to a mercury bubbler, are placed powdered pyridinium chlorochromate (26 g, 120 mmol) and methylene chloride (200 mL). To the well-stirred suspension, a solution of trioctylaluminum in THF thus prepared was added with the aid of a double-ended needle. The mixture was stirred at room temperature for 1 h. Then, ethyl ether (200 mL) was added and the mixture was filtered through a column containing Florisil®. The solid residue in the flask was triturated with ethyl ether (3×50 mL) and filtered through the same Florisil column. The combined filtrate was concentrated and distilled to afford 6.04 g of pure octanal (78%); bp 170-172 °C/761 mmHg. The purity was further confirmed by GC analysis.

A small scale of same reaction (trioctylaluminum, 1 mmol) was also performed and tridecane was added as an internal standard. The product aldehyde was analyzed by GC with use of a Carbowax TAP capillary column (25 m) to show 97% octanal formation.

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## References

1. Present address: Kyongsang Buk-Do, Provincial Government Institute of Health and Environment, Taegu 702-702, Korea.
2. Brown, H. C.; Kulkarni, S. V.; Rao, C. G. *Synthesis* **1979**, 702.
3. (a) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1464. (b) Yoon, N. M.; Brown, H. C. *ibid.* **1968**, *90*, 2927.
4. Cha, J. S.; Brown, H. C. *J. Org. Chem.* **1993**, *58*, 3974.
5. The solution of aluminum hydride in THF was prepared from the reaction of lithium aluminum hydride with methanesulfonic acid. See, ref. 4.

# The Synthesis of a New Pyrazolylimidazolinone *via* 1,3-Dipolar Cycloaddition Reaction of *N*-Methyl Sydnone with Methyl Propiolate

**Dong Ju Jeon, Jung No Lee, Hyoung Rae Kim, and Eung K. Ryu***

*Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Taejon 305-606, Korea*
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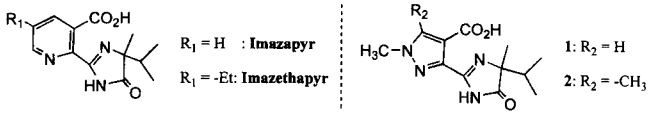
Herbicides having imidazolinone moiety, such as *imazapyr* and *imazethapyr*, have attracted much attention as a potent herbicidal activity, inhibiting branched chain amino acid biosynthesis.[1] In search for new structures with good biological activities, we have extensively studied on the modification of *imazapyr* and designed the pyrazolylimidazolinone (**1**) as a target molecule (Scheme 1).

Although the compound **2** ($R_2$=$CH_3$) had already been reported,[2] we expected that the compound **1** ($R_2$=H) would show better herbicidal effect than **2** due to the structure-activity correlation calculations.[3]

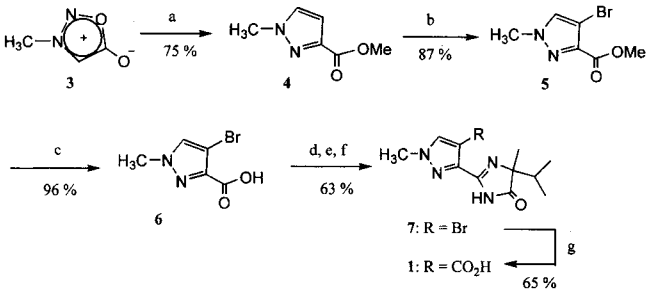
As we realized that it was difficult for the synthesis of **1** by the route employed in the synthesis of **2**, we explored a new procedure using 1,3-dipolar cycloaddition reaction of *N*-methylsydnone (**3**) with methyl propiolate.

It have been known that sydnones, known as meso-ionic heterocycles,[4] undergo well 1,3-dipolar cycloaddition reaction with alkyl propiolates to give pyrazoles of two possible regioisomers and 3-pyrazolecarboxylate is predominantly formed over 4-pyrazolate.[5]

When a mixture of *N*-methylsydnone (**3**) and methyl propiolate were refluxed in toluene for 12h,[6] only methyl 1-methyl-3-pyrazolecarboxylate was obtained with good regioselectivity in 75% yield. We conceived the product of dipolar cycloaddition reaction is methyl 1-methyl-3-pyrazolecarboxylate of possible two regioisomers, methyl 1-methyl-3-pyrazolecarboxylate and methyl 1-methyl-4-pyrazolecarboxylate, by its appropriate coupling of two protons ($J$=2.5 Hz) at the pyrazole ring in $^1$H NMR spectrum.




**Scheme 1**




**Scheme 2.** *Reagents and conditions*: [a] methyl propiolate, toluene, reflux, 12h. [b] NBS/$CHCl_3$, reflux, 5h. [c] LiOH/MeOH/$H_2O$, rt, overnight. [d] $SOCl_2$, reflux, 3h. [e] $H_2N$-(2-amino-2-oxoethyl), $CH_3CN$. [f] NaOH/EtOH/$H_2O$, reflux, 2h. [g] 2.2 eq. n-BuLi/THF, −78 °C, 20 min, then, $CO_2$, −78 °C, rt.

Compound **4** could be converted to 4-bromopyrazole **5** with good regioselectivity. This conversion which was confirmed by the disapperence of the peak at 6.82 ppm in $^1$H NMR of **4** was carried out by treatment with NBS in chloro-