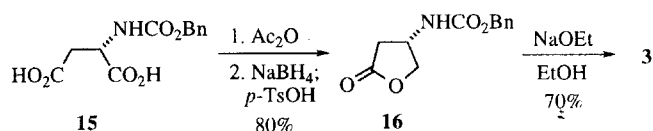


- Lhommet, G. *Heterocycles* **1990**, *31*, 1251. (c) Paulvannan, K.; Stille, J. R. *J. Org. Chem.* **1994**, *59*, 1613.
3. (a) Nagao, Y.; Dai, W.-M.; Ochiai, M.; Tsukagoshi, S.; Fujita, E. *J. Am. Chem. Soc.* **1989**, *110*, 289. (b) Nagao, Y.; Dai, W.-M.; Ochiai, M.; Tsukagoshi, S.; Fujita, E. *J. Org. Chem.* **1990**, *55*, 1148. (c) Gage, J. L.; Branchaud, B. P. *Tetrahedron Lett.* **1997**, *38*, 7007.
4. Ha, D.-C.; Kil, K.-E.; Choi, K.-S.; Park, H.-S. *Tetrahedron Lett.* **1996**, *37*, 5723.
5. (a) McGarvey, G. J.; Williams, J. M.; Hiner, R. N.; Matsumura, Y.; Oh, T. *Tetrahedron Lett.* **1983**, *24*, 2733. (b) McGarvey, G. J.; Williams, J. M.; Hiner, R. N.; Matsumura, Y.; Oh, T. *J. Am. Chem. Soc.* **1986**, *108*, 4943.
6. In our previous communication, we reported the specific rotation of **4** to be +8.5 (c 2.4, CHCl₃).⁴ But, we found partial racemization observed during the removal of acetic acid under elevated temperature after the anhydride formation from **15**. Evaporation with dioxane below 40 °C under reduced pressure to remove acetic anhydride and acetic acid provided optically pure anhydride which was reduced to **16**.^{5b} Lactone **16** was converted to oxazolidinone **3**, and the specific rotation of **4** from **3** was +11.7 (c 2.4, CHCl₃).



7. Spectroscopic data for **5**: colorless oil; $R_f=0.60$ (EtOAc); $[\alpha]_D^{20}=+100.9$ (c 0.54, CHCl₃); IR (CH₂Cl₂, cm⁻¹) 1748, 1437, 1231; ¹H NMR (300 MHz, CDCl₃) δ 4.54 (dd, $J=9.2, 8.2$ Hz, 1H), 4.16 (q, $J=7.1$ Hz, 2H), 4.06 (dd, $J=9.2, 6.4$ Hz, 1H), 3.89 (m, 1H), 3.78 (m, 1H), 2.80 (m, 1H), 2.31 (m, 2H), 1.78 (m, 1H), 1.52 (m, 2H), 1.26 (t, $J=7.1$ Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 14.1, 23.6, 26.4, 40.8, 46.4, 55.3, 61.2, 67.7, 156.7, 171.8; HRMS m/z calcd. for C₁₀H₁₅NO₄ 213.1001, found 213.1002. **6**: colorless oil; $R_f=0.36$ (EtOAc); $[\alpha]_D^{20}=+10.5$ (c 0.44, CHCl₃); IR (CH₂Cl₂, cm⁻¹) 1744, 1439, 1244; ¹H NMR (300 MHz, CDCl₃) δ 4.36 (t, $J=9.1$ Hz, 1H), 4.14 (m, 3H), 3.95-3.82 (m, 2H), 2.85 (dt, $J=12.4, 4.0$ Hz, 1H), 2.66 (m, 1H), 2.16 (m, 1H), 1.82-1.63 (m, 2H), 1.49 (m, 1H), 1.23 (t, $J=7.1$ Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 13.4, 19.1, 25.2, 39.9, 40.1, 53.6, 59.9, 64.5, 156.2, 171.0; HRMS m/z calcd. for C₁₀H₁₅NO₄ 213.1001, found 213.1001.

Conversion of Carboxylic Acids into Aldehydes by Oxidation of Alkoxyaluminum Intermediate with Pyridinium Chlorochromate or Pyridinium Dichromate

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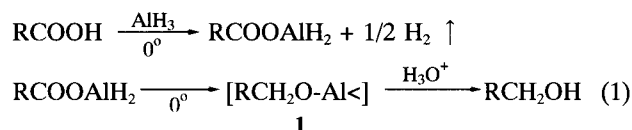
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Received April 8, 1998

Very recently, we reported that primary and secondary alcohols are readily converted into the corresponding aldehydes and ketones in essentially quantitative yields by oxidation of trialkoxyaluminum with pyridinium chlorochromate (PCC) at room temperature.¹ The reaction proceeds in a similar fashion where alcohols are converted into carbonyl compounds by oxidation of trialkyl borates with PCC,² however the reaction conditions appear to be much milder presumably due to the bigger atomic size of aluminum than that of boron. From this point of view, we decided to extend this procedure to the transformation of carboxylic acids into the corresponding aldehydes, similar to the case in which carboxylic acids are converted into aldehydes by oxidation of trialkoxyboroxine with PCC.³

Carboxylic acids are readily reduced to the corresponding alcohols with immediate evolution of 1 equiv hydrogen by aluminum hydride at 0 °C⁴ (Eq. 1). The initial reaction product in such reduction has not been identified, but we believe that it could be a kind of alkoxyaluminum (**1**). As the facile conversion of primary alcohols to aldehydes by ox-



idation of trialkoxyaluminum by PCC as already reported,¹ we undertook to explore the practicality of a simple one-pot conversion of carboxylic acids into aldehydes. Herein, we describe such transformation by oxidation of the alkoxyaluminum intermediate (**1**) with PCC or pyridinium dichromate (PDC).

The method involves the rapid reduction of carboxylic acid with aluminum hydride, followed by oxidation of the resultant alkoxyaluminum intermediate (**1**) (without isolation) with PCC or PDC at room temperature (Eq. 2).

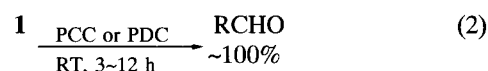


Table 1. Conversion of Carboxylic Acids to Aldehydes by Oxidation of Alkoxyaluminum Intermediate (1) with Pyridinium Chlorochromate (PCC) or Pyridinium Dichromate (PDC) at Room Temperature^a

Acid	Product	Reaction time(h)	PCC ^b	PDC ^b
			Yield (%) ^c	Yield (%) ^c
Hexanoic	Hexanal	12	96(82)	94(76)
Decanoic	Decyl aldehyde	12	95	96
Pentadecanoic	Pentadecyl aldehyde	12	97	94
Isobutyric	Isobutyraldehyde	12	94	92
Trimethylacetic	Trimethylacetaldehyde	12	95	93
Cyclopentanecarboxylic	Cyclopentanecarboxaldehyde	12	95	94
Cyclohexanecarboxylic	Cyclohexanecarboxaldehyde	12	96	95
Diphenylacetic	Diphenylacetaldehyde	12	94	92
6-Bromohexanoic	6-Bromohexanal	12	96	95
Cinnamic	Cinnamaldehyde	12	95	98
Benzoic	Benzaldehyde	6	99(85)	99
1-Naphthoic	1-Naphthaldehyde	12	98	98
<i>o</i> -Toluic	<i>o</i> -Tolualdehyde	6	99	99
<i>m</i> -Toluic	<i>m</i> -Tolualdehyde	6	98	99
<i>p</i> -Toluic	<i>p</i> -Tolualdehyde	6	99	99
<i>p</i> -Anisic	<i>p</i> -Anisaldehyde	6	98	98
4-Chlorobenzoic	4-Chlorobenzaldehyde	6	99.5	98
4-Nitrobenzoic	4-Nitrobenzaldehyde	6	99	96

^a In a tetrahydrofuran-methylene chloride mixture solvent. ^b Reacted with 10% excess oxidant. ^c GC yields. The numerals in parentheses are isolated yields.

As listed in Table 1, this procedure provides a clean, convenient conversion. There is actually no difference in yields of aldehydes between oxidants applied, PCC and PDC. It converts aliphatic carboxylic acids to aldehydes in yields of 92-97%. Alicyclic derivatives, such as cyclopentanecarboxylic acid and cyclohexanecarboxylic acid, work equally well. Derivatives are readily accommodated. Thus, diphenylacetic acid yields the corresponding aldehyde in yields of 92-94%. Similarly, 6-bromohexanoic acid is readily converted to the aldehyde in yields of 95-96%. α,β -Unsaturated acids, such as cinnamic acid, are also readily converted to the corresponding α,β -unsaturated aldehydes in essentially quantitative yields.

The conversion of aromatic acids into the corresponding aldehydes with this procedure is also essentially quantitative. The oxidation of aromatic intermediate is much faster than that of aliphatic one: it requires only 3-6 h at room temperature. Although PDC is more reactive than PCC, there is no bias toward oxidizing agents examined in giving quantitative yields of aldehydes.

This reaction is broadly applicable, tolerating many substituents, such as halogeno, methoxy, nitro, and alkene groups. The reactivity of aluminum hydride toward a carboxylic acid function and of PCC and PDC toward alkoxyaluminum intermediate (1) provides much milder reaction conditions, compared to the procedure in which borane-methyl sulfide (BMS) is involved.³ Moreover, PCC and PDC are reagents of choice: the problem caused by the acidic nature of PCC can be largely eliminated by using the more neutral reagent PDC.⁵ Consequently, this method provides another convenient procedure for the direct conversion of carboxylic acids to the corresponding aldehydes.⁶ The following procedure for the reaction of hexanoic acid is representative. An oven-dried, 250-mL, round-bottom flask with sidearm, equipped with a magnetic stirring bar and a reflux condenser, was attached to a mercury bubbler. The flask was flushed

with dry nitrogen and then maintained under a static pressure of nitrogen. The flask was charged with hexanoic acid (6.97 g, 60 mmol) and 30 mL of THF. The flask was immersed in an ice-water bath and a precooled 1.0 M solution of aluminum hydride⁷ (30 mL, 30 mmol) in THF was added dropwise with vigorous stirring. After the complete evolution of the hydrogen, the ice-water bath was removed and the reaction mixture was stirred for 30 min at room temperature.

To a well-stirred suspension of pyridinium chlorochromate (14.3 g, 66 mmol) in methylene chloride (100 mL) taken in a 500-mL flask equipped as described above, is added dropwise the above solution of alkoxyaluminum intermediate in THF using a cannula. The mixture was stirred for 12 h at room temperature. The small portion of this mixture was transferred to a vial and dodecane was added as an internal standard. GC analysis using a Carbowax 20 M capillary column (20 m) showed the presence of hexanal in a yield of 96%. The reaction mixture was diluted with 200 mL of diethyl ether and the supernatant liquid is filtered through Florisil[®] (100 g) contained in a 300-mL sintered glass funnel. The solid residue is washed with diethyl ether (3 \times 50 mL) and passed through the same Florisil column. The filtrate was concentrated and distilled to afford pure hexanal (4.93 g, 82% yield); b.p. 129-130 °C (754 mmHg).

Analogous procedures are 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 except the oxidation time.

Acknowledgment. The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1997.

References

1. Cha, J. S.; Kim, M. G.; Kim, J. M.; Kwon, O. O.; Chun,

- J. H.; Cho, S. D. *Bull. Korean Chem. Soc.* **1998**, 7, 000.
2. Brown, H. C.; Kulkarni, S. U.; Rao, C. G. *Synthesis* **1979**, 702.
 3. Brown, H. C.; Rao, C. G.; Kulkarni, S. U. *Synthesis* **1979**, 704.
 4. (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. (c) Cha, J. S.; Brown, H. C. *J. Org. Chem.* **1993**, 58, 3974.
 5. Smith, M. B. *Organic Synthesis: Theory, Reactions, and Methods*; McGraw-Hill Book Co.: New York, 1994.
 6. (a) Brown, H. C.; Cha, J. S.; Nazer, B.; Yoon, N. M. *J. Am. Chem. Soc.* **1984**, 106, 8001. (b) Brown, H. C.; Cha, J. S.; Yoon, N. M.; Nazer, B. *J. Org. Chem.* **1987**, 52, 5400. (c) Cha, J. S.; Kim, J. E.; Oh, S. Y.; Lee, J. C.; Lee, K. W. *Tetrahedron Lett.* **1987**, 28, 2389. (d) Cha, J. S.; Kim, J. E.; Lee, K. W. *J. Org. Chem.* **1987**, 52, 5030. (e) Cha, J. S.; Kim, J. E.; Oh, S. Y.; Kim, J. D. *Tetrahedron Lett.* **1987**, 28, 4575. (f) Cha, J. S.; Kim, J. E.; Yoon, M. S.; Kim, Y. S. *Ibid.* **1987**, 28, 623. (g) Cha, J. S.; Oh, S. Y.; Lee, K. W.; Yoon, M. S.; Lee, J. C.; Kim, J. E. *Bull. Korean Chem. Soc.* **1988**, 9, 48. (h) Cha, J. S.; Oh, S. Y.; Lee, K. W.; Yoon, M. S.; Lee, J. C.; Kim, J. E. *Heterocycles* **1988**, 27, 1595. (i) Cha, J. S.; Lee, K. W.; Yoon, M. S.; Lee, J. C. *Bull. Korean Chem. Soc.* **1988**, 9, 384. (j) Cha, J. S.; Lee, J. C.; Yoon, M. S.; Seo, J. B.; Kim, J. M. *Ibid.* **1990**, 11, 76. (k) Cha, J. S. *Ibid.* **1992**, 13, 670. (l) Muraki, M.; Mukaiyama, T. *Chemistry Lett.* **1974**, 1447. 1975, 215, 875. (m) Hubert, T. D.; Eyman, D. P.; Wiemer, D. F. *J. Org. Chem.* **1984**, 49, 2279. (n) Cha, J. S.; Lee, K. D.; Kwon, O. O.; Kim, J. M.; Lee, H. S. *Bull. Korean Chem. Soc.* **1995**, 16, 561. (o) Cha, J. S.; Chang, S. W.; Kim, J. M.; Kwon, O. O.; Lee, J. C. *Org. Prep. Proced. Int.* **1997**, 29, 665.
 7. Aluminum hydride was prepared by the reaction of lithium aluminum hydride and methanesulfonic acid. See, ref. 4-c.