126.83 (10 + 14), 129.32 (11 + 13), 135.69 (12), 139.27 (2), 143.40 (9), 207.15 (4); *m/e* 216 (M$^+$, 47), 119 (93), 83 (100), 55 (20).

***ar*-Turmerone (8).** Iso-*ar*-turmerone (7) (0.96 g, 4.4 mmol) and a catalytic amount of piperidine[25] (130 μL) in 10 mL of Et$_2$O were stirred for 64 h at room temperature. Workup afforded 0.92 g (95%) of *ar*-turmerone (8). The infrared and ^{1}H NMR spectra were identical with those reported in the literature.[7,8] The mass spectrum was essentially the same as that for iso-*ar*-turmerone: ^{13}C NMR (CDCl$_3$) δ (C numbering of formula 8, Scheme II) 20.64 (8), 20.95 (15), 22.04 (7), 27.50 (1), 35.39 (6), 52.76 (5), 124.28 (3), 126.83 (10 + 14), 129.19 (11 + 13), 135.45 (12), 143.83 (9), 154.63 (2), 199.50 (4).

Registry No. 1, 70369-23-2; **2**, 70369-24-3; **3**, 59204-74-9; **4**, 539-52-6; **5**, 70369-25-4; **6**, 70369-26-5; **7**, 70369-27-6; **8**, 532-65-0; **9**, 70369-28-7; **10**, 70369-29-8; 3-cyanofuran, 30078-65-0; ethyl 3-furanthiocarboximidate hydrochloride, 70369-30-1; prenyl bromide, 870-63-3; ethyl bromide, 74-96-4; 2-(4-methylphenyl)propyl bromide, 23430-51-5; β-methallyl chloride, 1458-98-6.

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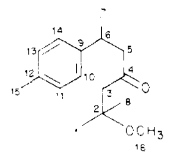
(25) Isomerization of the double bond with sodium hydroxide in methanol afforded 8 and a 1,4 addition product **10**: IR (film) 1702 (C═O),



10

1510, 811 (aromatic), 2822 and 1072 (OCH$_3$) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.11 (m, 9 H), 2.22 (s, 3 H), 2.31 (s, 2 H), 2.59 (m, 2 H), 2.87–3.58 (m, 1 H), 3.05 (s, 3 H), 6.93 (s, 4 H); ^{13}C NMR (CDCl$_3$) δ (multiplicity determined by an off-resonance study) 20.95 (q, 15), 22.10 (q, 7), 24.83 (q, 1 + 8), 34.91 (d, 6), 49.12 (q, 16), 53.37 (t, 3 + 5), 74.31 (s, 2), 126.89 (10 + 14), 129.25 (11 + 13), 135.57 (12), 143.64 (9), 208.36 (4); *m/e* 216 (45), 119 (86), 83 (100), 32 (15), 31 (19).

Stoichiometry of the Oxidation of Primary Alcohols with Pyridinium Chlorochromate. Evidence for a Two-Electron Change

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The oxidation of secondary alcohols to ketones with aqueous chromic acid has long been a standard synthetic procedure.[2,3] Primary alcohols, under similar conditions, produce esters.[4] The oxidation of primary alcohols with Collins' reagent, however, affords the desired aldehydes in moderate yields.[5] Pyridinium chlorochromate (PCC) oxidizes a wide variety of alcohols to carbonyl compounds with high efficiency.[6] The reaction involves simply the addition of alcohols to a well-stirred suspension of PCC in methylene chloride.

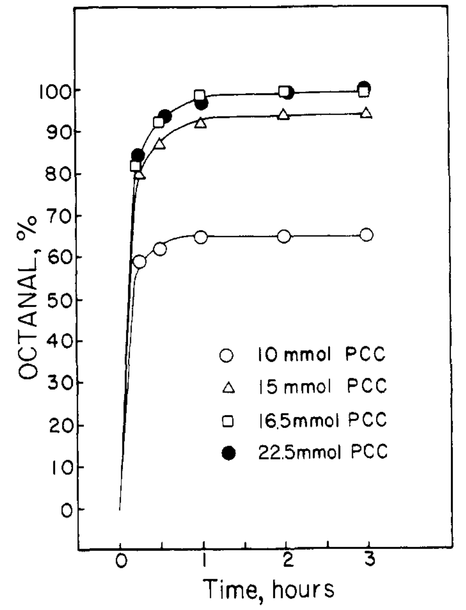

Figure 1. Oxidation of 15.0 mmol of 1-octanol with different quantities of PCC in 15 mL of refluxing methylene chloride.

Extensive kinetic and mechanistic studies on the oxidation of alcohols with chromic acid have revealed that such reactions ordinarily involve a three-electron change, whereby the oxidant, Cr(VI) species, is reduced to Cr(III).[2,7,8] Although PCC has been widely used since its discovery, no systematic study of the stoichiometry of PCC oxidation is reported in the literature.[9,10] Therefore, in connection with our studies on the oxidation of organoboranes with this reagent,[11] we undertook to examine the stoichiometry in the oxidation of a representative alcohol.

In a typical experiment, 15 mmol of 1-octanol was added to a well-stirred suspension of varying amounts (10, 15, 16.5, and 22.5 mmol) of PCC in 15 mL of methylene chloride, and the mixture was heated under reflux. The progress of the reaction was followed by analyzing the reaction mixture for octanal by GC (Figure 1).

It is evident from Figure 1 that when 10 mmol of PCC is used, the stoichiometric amount of reagent assuming a three-electron change, 9.4 mmol of the aldehyde (64%) is produced. On the other hand, use of 15 mmol of PCC, the stoichiometric amount of reagent assuming a two-electron change, forms 14.1 mmol of aldehyde, a yield of 94%. Both 16.5 and 22.5 mmol of PCC afford a quantitative yield (by GC) of octanal. Considering the purity of commercial PCC (Aldrich, 98% specified), it appears that 15 mmol is the theoretical amount required to oxidize 15 mmol of 1-octanol to octanal. Use of 22.5 mmol, the amount used by the original authors,[6] appears to be unnecessary. Therefore, we conclude that the oxidation of primary alcohols to aldehydes by PCC under the conditions employed involves the transfer of only two electrons, contrary to the three-electron transfers observed in aqueous chromic acid oxidations

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[1] (a) Postdoctoral research associate on a grant from Exxon Research and Engineering Co.; (b) postdoctoral research associate on Grant No. GM 10937-16 from the National Institutes of Health.

[2] For a review, see: Wiberg, K. B. "Oxidation in Organic Chemistry", Part A; Academic Press: New York, 1965; pp 69–184.

[3] (a) Beckmann, P. *Justus Liebigs Ann. Chem.* **1880**, *250*, 322. (b) Sandborn, L. T. "Organic Syntheses", Collect.; Wiley: New York, 1947; Vol. I, p 340. (c) Brown, H. C.; Garg, C. P. *J. Am. Chem. Soc.* **1961**, *83*, 2952.

[4] Robertson, G. R. ref 3b, p 138.

[5] Collins, T. C.; Hess, W. W.; Frank, F. J. *Tetrahedron Lett.* **1968**, 3363.

[6] Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

[7] Wiberg, K. B.; Mukherjee, S. K. *J. Am. Chem. Soc.* **1971**, *93*, 2543; and the references therein.

[8] Roček, J.; Radkowsky, A. E. *J. Am. Chem. Soc.* **1973**, *95*, 7123.

[9] The original workers[6] employed 1.5 molar equiv of PCC. Others have followed this procedure. There is one report on the kinetic studies of PCC oxidation in a nitrobenzene–methylene chloride mixture where the three-electron transfer has been proposed.[10] But those conditions are different from usual experimental conditions employed in the oxidation of alcohols.

[10] Banerjee, K. K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2732.

[11] Rao, C. G.; Kulkarni, S. U.; Brown, H. C. *J. Organomet. Chem.* in press.

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$$RCH_2OH + C_5H_5N\cdot HCl\cdot CrO_3 \rightarrow RCHO + C_5H_5N\cdot HCl + CrO_2 + H_2O \quad (1)$$

The precise nature of the reduced chromium product has not been investigated. Presumably, it is chromium dioxide or some intermediate formed from pyridinium chloride and chromium dioxide. Some examples of two-electron oxidations with the Cr(VI) compound have been reported in the past. Oxidation with chromyl chloride involves such a two-electron transfer.[12] Even in the oxidation of isopropyl alcohol with chromic acid, the chromium(IV) species once formed is completely inert as an oxidant in the absence of at least a minimal amount of water.[7]

This work represents the first report of a stoichiometric study in the oxidation of alcohols with pyridinium chlorochromate and reveals that it involves a two-electron change. The alcohols can be oxidized in refluxing dichloromethane utilizing only the theoretical amount of pyridinium chlorochromate.[13]

Experimental Section

The gas chromatographic analyses were carried out on a Varian-1400 instrument using a 8 ft × 1/8 in. column packed with 5% SE-30 deposited on Varaport-30. Pyridinium chlorochromate (labeled 98% pure) and methylene chloride (Gold Label) from Aldrich Chemical Co. were used without further purification. 1-Octanol from Aldrich was distilled from calcium hydride prior to use.

Reaction of 1-Octanol with Pyridinium Chlorochromate. In an oven-dried, nitrogen-flushed, 100-mL, round-bottom flask, equipped with a magnetic stirring bar, a septum inlet, reflux condenser, and a connecting tube leading to a mercury bubbler, were placed 2.16 g (10 mmol) of PCC, 15 mL of CH_2Cl_2, and 1.3 mL (5 mmol) of *n*-tetradecane (internal standard for GC analysis). To the well-stirred mixture was added 2.36 mL (15 mmol) of 1-octanol, and the mixture was heated under reflux. At definite intervals of time, 0.5 mL of the supernatant liquid was withdrawn and added to a vial containing 2 mL of ether in order to quench the reaction. The clear ether solution was analyzed by GC for the amount of octanal.

The experiments were repeated with 3.24 (15 mmol), 3.56 (16.5 mmol), and 4.86 g (22.5 mmol) of PCC.

Registry No. PCC, 26299-14-9; 1-octanol, 111-87-5; octanal, 124-13-0.

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[12] (a) Wiberg, K. B.; Lepse, P. A. *J. Am. Chem. Soc.* **1961**, *86*, 2612. (b) Makhija, R. C.; Stairs, R. A. *Can. J. Chem.*, **1968**, *46*, 1255. (c) Makhija, R. C.; Stairs, R. A. *ibid.* **1969**, *47*, 2293.

[13] A referee of this manuscript has suggested that under the more usual reaction conditions, dichloromethane at 25 °C, a larger excess, approximately 1.5 molar equiv, is required, probably because of some entrapment of PCC in the reduced chromium tars formed during the reaction.

Metal-Ammonia Cleavage of Esters to Alcohols

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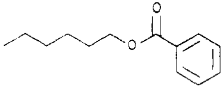
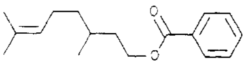
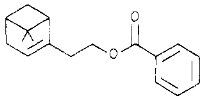
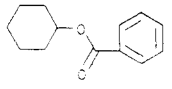
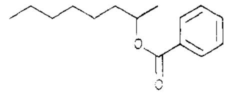
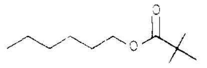
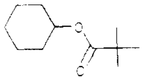
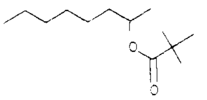
A common protecting group for alcohols is the ester since this group is easy to prepare and offers good stability toward acid. The alcohol is recovered either by saponification, hydride reduction, or reaction with organometallic reagents.[1] Removal of an ester protecting group with base often requires relatively harsh conditions particularly with esters derived from aromatic acids or hindered acids. On the other hand, deprotection with lithium aluminum hydride is limited because of the lack of selectivity of this most reactive reagent while organometallics also react with a wide variety of functional groups.

Table I. Cleavage of Esters to Alcohols

ester	metal[a]	alcohol % yield (yield in g)[b]
	Li	84 (4.28)
	Li	85 (2.67)
	Li	84 (2.80)
	Li	78 (3.90)
	Na	97 (2.52)
	Li	71 (3.63)
	Li	79 (3.95)
	Li	85 (2.22)

[a] Six equivalents of the metal is used.[5] [b] All yields refer to isolated alcohols-pure by TLC, IR, and NMR. The products are distilled to remove benzyl or neopentyl alcohol.

We report a procedure for the cleavage of esters that uses either sodium or lithium in ethereal ammonia (eq 1).[2-5]

$$ROOCR' \xrightarrow[NH_3]{\text{Na or Li}} \xrightarrow{NH_4Cl} ROH + (R'CH_2OH) \quad (1)$$

Benzoate and pivalate esters of both primary and secondary alcohols are reduced efficiently (see Table I). For example, the benzoate and pivalate esters of 1-hexanol are

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[1] C. B. Reese in "Protective Groups in Organic Chemistry", J. F. W. McOmie, Ed., Plenum Press, New York, 1973, pp 109–118.

[2] There are two familiar reactions in which an ester is allowed to react with a metal—namely, the Bouveault–Blanc reduction (see H. O. House, "Modern Synthetic Reactions", 2nd ed., W. A. Benjamin, Menlo Park, Calif., 1972, pp 150–151) and the acyloin condensation (see J. J. Bloomfield, D. C. Owsley, and J. M. Nelke, *Org. React.* **23**, 259 (1976)); however, the focus in both of these reactions is the acid portion of the ester. Two papers which deal with the fate of the alcohol portion of esters after metal reduction have appeared recently.[3,4]

[3] Lithium in ethylamine reduces esters of hindered alcohols to alkanes: R. B. Boar, L. Joukhadar, J. F. McGhie, S. C. Misra, A. G. M. Barrett, D. H. R. Barton, and P. A. Prokopiou, *J. Chem. Soc., Chem. Commun.*, 68, (1978).

[4] Sodium in hexamethylphosphoramide reduces the esters of tertiary alcohols to alkanes; however, esters of primary or secondary alcohols are reduced to a mixture of both the alkane and the alcohol: H. Deshayes and J.-P. Pete, *J. Chem. Soc., Chem. Commun.*, 567 (1978).

[5] Cleavage of benzoates gives benzyl alcohol as a side product. Benzylic alcohols yield alkanes when allowed to react with lithium in ammonia—for example, see S. S. Hall and F. J. McEnroe, *J. Org. Chem.*, **40**, 271 (1975). Consequently, using *n*-hexyl benzoate, the metal to ester ratio was varied from 4 to 36. A ratio of 6 to 1 proved to give the best yields of 1-hexanol with minimal benzyl alcohol.

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