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

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 At definite intervals of time, 0.5 mL of the supernatant liquid was withdrawn and added to a vial containing 2 mL of ether in order to quench the reaction.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.

(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

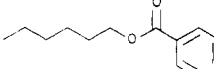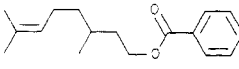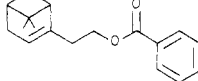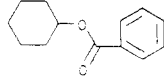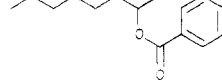Harold W. Pinnick* and Elina Fernandez

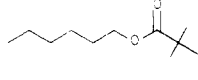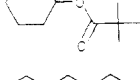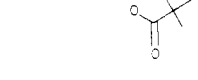*Department of Chemistry, University of Georgia, Athens, Georgia 30602*

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

(1) C. B. Reese in "Protective Groups in Organic Chemistry", J. F. W. McOmie, Ed., Plenum Press, New York, 1973, pp 109–118.
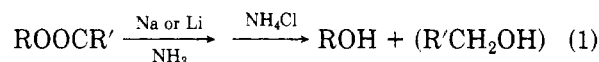
Table I. Cleavage of Esters to Alcohols

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.

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.

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

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

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

(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; 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.

reduced in 84 and 71% yields, respectively. Lithium and sodium each reduce all the esters studied but only the higher yield for each ester is provided in the table. As an illustration, n-hexyl benzoate is cleaved by lithium in 88% yield whereas sodium gives a 74% yield on the same scale, but the difference between the two metals is frequently even less than in this case. These reaction conditions are also effective for cleaving acetates. For example, n-hexyl acetate gives an 88% yield of 1-hexanol while cyclohexyl acetate is cleaved in 83% yield.

Because of the success with pivalate esters, other hindered esters were subjected to the reductive conditions. Indeed, n-hexyl mesitoate is cleaved by lithium to give 1-hexanol, as determined by VPC analysis, contaminated with 2,4,6-trimethylbenzyl alcohol and isodurene. Unfortunately, the highly sterically hindered tert-butyl mesitoate did not react with lithium in ammonia under the reaction conditions described (65% of the ester was recovered from a single small-scale experiment). Consequently, it appears that this method will not cleave extremely hindered esters.

The reaction suffers from two additional limitations. The esters of allylic alcohols give alkyl oxygen cleavage.[3,4] Thus, the benzoate ester of geraniol gives only a trace of alcohol when reduced with either sodium or lithium. The major product is 2,6-dimethyl-2,6-octadiene in 65–75% yield. In addition, sodium or lithium destroys the benzoate ester of tetrahydrofurfuryl alcohol to give products apparently derived from 1,2-elimination. Despite these minor limitations, this method should prove useful for the removal of many ester protecting groups.

Since the products of a metal–ammonia reduction are often affected by the presence of a proton donor in the quenching step,[6-8] the role of quenching agent was examined. When the reaction of n-hexyl benzoate with lithium is quenched with either sodium benzoate or 1,2-dichloroethane, the major products are 1-hexanol and benzyl alcohol as well as 5–10% of benzaldehyde. No toluene is produced. With n-hexyl pivalate, quenching with either sodium benzoate or 1,2-dichloroethane gives only 1-hexanol and neopentyl alcohol. Consequently, a proton source is not necessary for the liberation of the alcohol so that metal–ammonia reducible groups requiring proton sources for reduction will be unaffected, thus improving the selectivity of this deprotection method.[9] A typical experimental procedure follows.[10]

Cleavage of n-Hexyl Benzoate

A solution of the ester (4.12 g, 20.0 mmol) in 30 mL of ether was added over a 10-min period to a vigorously stirred blue solution of 0.83 g (0.12 g-atom, 6.0 equiv) of lithium in 250 mL of ammonia. The blue color persisted during 2 h of additional stirring. The reaction was quenched with ammonium chloride, the ammonia was allowed to escape, and 50 mL of water and 50 mL of ether were added. The two-phase mixture was stirred for 30 min and separated. The aqueous phase was extracted with three 20-mL portions of ether. The combined ether layers were washed with two 50-mL portions of water, dried over anhydrous $MgSO_4$, and concentrated to give, after distillation, 1.80 g (88.2%)

of pure 1-hexanol: bp 55–60 °C (20 torr); NMR (CCl_4, δ) 0.9 (skewed t, 3 H), 1.4 (m, 8 H), 2.8 (br s, 1 H), 3.5 (t, $J = 6$ Hz, 2 H).

Structure of Moronic Acid[1]

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Recent studies of *Roylea elegans* Wall have led to the isolation of two furanoid diterpene isomers,[2] royeleganin and royelegafuran. A further investigation of this plant has yielded a new triterpene, named herewith moronic acid, the determination of whose structure forms the subject of the present communication.

The $C_{30}H_{46}O_3$ substance revealed infrared absorption bands at 1715, 1697, and 1668 cm^{-1} characteristic of a six-membered ring ketone, a carboxylic acid, and a carbon–carbon double bond, respectively, and ^{1}H NMR spectra with three-proton singlets at 0.80, 0.96, 0.99, 1.01, 1.04, 1.04, and 1.09 ppm, a two-proton multiplet at 2.40 ppm, and a one-proton singlet at 5.18 ppm corresponding to seven methyl groups on nonprotonated carbon sites, an α-keto methylene group, and an olefinic methine attached to nonprotonated carbons, respectively. These data were suggestive of an olefinic keto acid structure of the amyrin type and were supported by the mass spectral fragmentation pattern of the natural product. The latter pinpointed the keto group at C(3), required the carboxy substituent to be located at C(17), and favored trigonality for C(18) and C(19) (especially in view of the appearance of the m/e 410 fragment).[3] Thus the formulation **1a** appeared to represent the structure of moronic acid.

A ^{13}C NMR spectral analysis was undertaken on methyl moronate (**1b**),[4] a soluble derivative of the natural acid, in order to confirm the structure assignment. The spectra confirmed all carbon types present in **1b** and revealed a close chemical shift resemblence of the ring A, B, and C carbons of the keto ester to those of lupeone.[5] Comparison

(6) (a) E. Wenkert and B. G. Jackson, *J. Am. Chem. Soc.*, **80**, 217 (1958); (b) M. L. Meyer and A. S. Levinson, *J. Org. Chem.*, **28**, 2184 (1963).

(7) Sodium benzoate quenches metal–ammonia reactions without the addition of a proton: S. S. Hall, S. D. Lipsky, and G. H. Small, *Tetrahedron Lett.*, 1853 (1971); S. S. Hall, S. D. Lipsky, F. J. McEnroe, and A. P. Bartels, *J. Org. Chem.*, **36**, 2588 (1971).

(8) 1,2-Dihaloethanes also quench metal–ammonia reactions without the addition of a proton: D. F. Taber, *J. Org. Chem.*, **41**, 2649 (1976).

(9) We thank a referee for helpful suggestions regarding the quenching agent.

(10) ^{1}H NMR spectra were recorded on a Varian T-60 instrument. IR spectra were obtained on a Perkin-Elmer Model 257 spectrometer.

(1) Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Naturally Occurring Substances. 64. Part 63: see M. Pais, F.-X. Jarreau, M. G. Sierra, O. A. Mascaretti, E. A. Ruveda, C.-J. Chang, E. W. Hagaman, and E. Wenkert, *Phytochemistry*, in press.

(2) P. L. Majumder and S. K. Panda, Abstracts, Convention of Chemists, CSIR, India, 1974, p Org-3; S. K. Panda, Ph.D. Thesis, Calcutta University, Calcutta, West Bengal, India, 1975; P. L. Majumder and S. K. Panda, "Symposium on the Chemistry, Biochemistry and Biogenesis of Natural Products", Calcutta University, 1975; Abstracts p A-11.

(3) H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 3688 (1963).

(4) Mp 166 °C (methanol); [α]_D 57° (c 4.3, $CHCl_3$); IR (KBr) C=O 1720, 1695 cm^{-1}; from diazomethane treatment of moronic acid.