Working with Hazardous Chemicals

The procedures in Organic Syntheses are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.
OXIDATION WITH THE CHROMIUM TRIOXIDE-PYRIDINE COMPLEX PREPARED in situ: 1-DECANAL

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\begin{align*}
\text{CH}_3(\text{CH}_2)_8 & \text{CH}_3\text{OH} & \text{CrO}_3 \cdot (\text{pyridine})_2 & \text{CH}_3(\text{CH}_2)_8 & \text{CHO} \\
\text{CH}_2\text{Cl}_2
\end{align*}
\]

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1. Procedure

A 3-l., three-necked, round-bottomed flask equipped with a stirrer, a thermometer, and a drying tube is charged with 94.9 g. (1.20 moles) of pyridine (Note 1) and 1.5 l. of dichloromethane (Note 2). The solution is stirred with ice-bath cooling to an internal temperature of 5°, and 60.0 g. (0.600 mole) of chromium trioxide (Note 3) is added in one portion. The deep burgundy solution is stirred in the cold for an additional 5 minutes, then allowed to warm to 20° over a period of 60 minutes. A solution of 15.8 g. (0.100 mole) of 1-decanol (Note 4) in 100 ml. of dichloromethane is added rapidly, with immediate separation of a tarry, black deposit. The reaction mixture is stirred for 15 minutes and decanted from the tarry residue, which is washed with three 500-ml. portions of diethyl ether. The combined organic solution is washed successively with three 1-l. portions of ice-cold, aqueous 5% sodium hydroxide, 1 l. of ice-cold, 5% hydrochloric acid, 1 l. of aqueous 5% sodium hydrogen carbonate, and 1 l. of saturated brine. The solution is dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure. The resulting pale yellow liquid is distilled through a 15-cm., vacuum-jacketed Vigreux column (Note 5), yielding 9.8–10.2 g. (63–66%, (Note 6) of 1-decanal, b.p. 96–98° (13 mm.) (Note 7).

2. Notes

1. Anhydrous pyridine was obtained by distillation of reagent grade material from barium oxide and storage over 4A molecular sieves.
2. Dichloromethane was purified by shaking with concentrated sulfuric acid, washing with aqueous sodium hydrogen carbonate and water, drying over anhydrous calcium chloride, and distilling. The purified solvent was stored in the dark over 4A molecular sieves.
3. Chromium trioxide (obtained from J. T. Baker Chemical Company) was stored in a vacuum desiccator over phosphorus pentoxide prior to use. Six-mole equivalents of oxidant is required for rapid, complete conversion to aldehyde. With less than the 6:1 molar ratio, a second, extremely slow oxidation step occurs (see reference 2).
4. 1-Decanol was obtained from Aldrich Chemical Company, Inc.
5. Vigorous magnetic stirring of the pot material prevents excessive foaming during the distillation.
6. The submitters obtained 12.9–13.0 g. (83%). The checkers obtained a yield of 66% when all solvent and wash volumes used in the procedure were reduced by 50%.
7. The product was identified through comparison of its IR, 1H NMR, and mass spectra and GC mobility with authentic 1-decanal, available from Aldrich Chemical Company, Inc.

3. Discussion

Dipyridine-chromium(VI) oxide\(^1\) was introduced as an oxidant for the conversion of acid-sensitive alcohols to carbonyl compounds by Poos, Arth, Beyler, and Sarett.\(^1\) The complex, dispersed in pyridine, smoothly converts secondary alcohols to ketones, but oxidations of primary alcohols to aldehydes are capricious.\(^5\) In 1968, Collins, Hess, and Frank found that anhydrous dipyridine-chromium(VI) oxide is moderately soluble in chlorinated hydrocarbons and chose dichloromethane as the solvent.\(^6\) With this modification, primary and secondary alcohols were oxidized to aldehydes and ketones in yields of 87–98%. Subsequently, Dauben, Lorber, and Fullerton showed that dichloromethane solutions of the
complex are also useful for accomplishing allylic oxidations.7

The chief drawbacks to using the Collins reagent are the nuisance involved in preparing pure dipyridine-chromium(VI) oxide,7 its hygroscopic nature,6 and its propensity to inflame during preparation.3,4,7 The present method avoids these difficulties by simply preparing dichloromethane solutions of the complex directly.2 In addition, as noted previously,6 the use of dichloromethane as solvent facilitates isolation of the products. Other modifications of the Collins procedure include the use of a celite-supported reagent which facilitates the isolation of sensitive products8 and the finding that a 1:1 pyridine-chromium trioxide ratio gives oxidation results9 comparable with those obtained using the customary 2:1 ratio in the in situ procedure.

Several other reagents finding utility for the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds under mild and nonaqueous conditions have been developed in recent years. Of the chromium(VI)-based oxidants, pyridinium chlorochromate10 in dichloromethane and pyridinium dichromate11 in N,N-dimethylformamide or dichloromethane deserve special mention. Both reagents are easily prepared and stored, allow the efficient oxidation of a variety of alcohols using only a modest excess of oxidant, and may be amenable to large-scale operations.

This preparation is referenced from:


References and Notes


Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

- brine
- calcium chloride (10043-52-4)
- sulfuric acid (7664-93-9)
- hydrochloric acid (7647-01-0)
- diethyl ether (60-29-7)
sodium hydroxide (1310-73-2)
sodium hydrogen carbonate (144-55-8)
barium oxide
pyridine (110-86-1)
dichloromethane (75-09-2)
magnesium sulfate (7487-88-9)
chromium trioxide (1333-82-0)
dimethylformamide (68-12-2)
1-Decanal (112-31-2)
1-decanol (112-30-1)
pyridinium chlorochromate (26299-14-9)
pyridinium dichromate (20039-37-6)
Dipyridine-chromium(VI) oxide
phosphorus pentoxide (1314-56-3)
pyridine-chromium trioxide