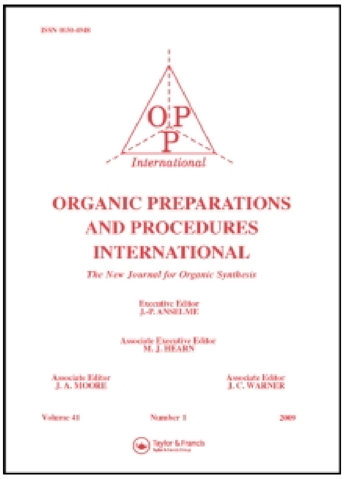

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DIRECT CONVERSION OF ALCOHOL TETRAHYDROPYRANYL ETHERS TO ALDEHYDES

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DIRECT CONVERSION OF ALCOHOL TETRAHYDROPYRANYL ETHERS TO ALDEHYDES

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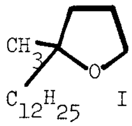
Pyridinium chlorochromate (PCC) in methylene chloride containing 1.2 equivalent of trifluoroacetic acid (TFA) is a useful reagent for the direct conversion of tetrahydropyranyl (THP) ethers to aldehydes (65-85% yields).[1,2] Presumably the ether is simply cleaved to the alcohol which is then oxidized. The preparation of 6-octadecenal illustrates the utility of this procedure.

$$RCH_2OTHP \xrightarrow[TFA]{PCC} RCHO \qquad (1)$$

$$C_{11}H_{23}CH=C(CH_3)CH_2CH_2CH_2OTHP \xrightarrow[TFA]{PCC}$$



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(2)

Although this procedure should prove compatible with a variety of functional groups such as esters, nitriles, ketones, alkynes and 1,2-disubstituted alkenes, characterizable products were generally not obtained from ethers containing trisubstituted olefinic linkages. An exception to this was the formation of 2-methyl-2-dodecyltetrahydrofuran (I) from 4-methyl-4-hexadecen-1-ol (Eq. 2).

Table 1.- Oxidation of Alcohol Tetrahydropyranyl Ethers to Aldehydes

THP ether	Product	Yield (%)
1-tetradecanol	tetradecanal	65
1-hexadecanol	hexadecanal	65
1-octadecanol	octadecanal	75
6-octadecen-1-ol	6-octadecenal	85
7,11-hexadecadiyn-1-ol	7,11-hexadecadiynal	75
4-methyl-4-hexadecen-1-ol	I	89

EXPERIMENTAL

Commercially available alcohols were employed directly; 7,11-hexadecadiyn-1-ol was prepared from its acetate (Farchan Chemical Co.) and 4-methyl-4-heptadecen-1-ol was synthesized by standard methods.[3] The alcohols were converted to tetrahydropyranyl ethers in the usual fashion.[4] Infrared (Beckman IR-10)[5] and pmr (Varian HA-100-A) data were obtained for all compounds and were in accord with assigned structures. Mass spectral data (Varian MAT CH5 Spectrometer) were obtained for the products of entries 4-6 and gas chromatograph comparisons (Hewlett-Packard 5730 instrument, 3.2 mm x 50 cm column of 10% UCW-982 on WAW-DMCS-Gas Chrom Q) were made with known samples of the aldehydes. Pyridinium chlorochromate was obtained from Aldrich Chemical Company.

<u>Synthesis of Aldehydes</u>.- A slurry of pyridinium chlorochromate (1.3 g, 6 mmoles) in methylene chloride (25 ml) was prepared and chilled in an ice bath. Trifluoroacetic acid (1.26 g, 6 mmoles) was injected into the mixture followed by addition of a solution of the alcohol-tetrahydropyranyl ether (5 mmoles) in methylene chloride (5 ml). The ice bath was removed and the deep red mixture stirred for 2 hrs. The mixture was diluted with ether (100 ml) and transferred to a separatory funnel. The viscous residue was washed with 2 ml of ether and the extract added to the funnel. The ethereal solution was washed with 50 ml of 5% NaOH which produced an aqueous layer of flocculent chromium salts. Failure to wash with base at this point resulted in chromium salts being carried through the subsequent column chromatography. The ethereal extract was dried ($MgSO_4$) and concentrated. The crude aldehyde was purified by passage through silica gel (25 g) eluting with 10% ethyl acetate in hexane (100 ml). The aldehydes were recovered by removal of the solvents and their identities assessed as noted. The products were of >95% purity (gas chromatography as noted).

In this manner were obtained tetradecanal, hexadecanal, octadecanal (glc comparison with known samples), as well as 7,11-hexadecadiynal:n_D^{21} 1.4710; ir (CCl_4) 2720 (CHO) and 1730 cm^{-1} (C=O); nmr (CCl_4) δ 2.2 (broad s, 4, $\equiv C-CH_2CH_2-C\equiv$) and 9.67 ppm (t, 1, J = 1,CHO); mass spectrum (70eV) m/e 232 (M^+), 204 ($M^+-C_2H_4$), 29 (HCO^+-), and 2-dodecyl-2-methyltetrahydrofuran: n_D^{21} 1.4552; ir (CCl_4) absence of OH and C=O, several bands 1000-1150 cm^{-1}; nmr (CCl_4) 63.6 ppm (m, 2, CH_2O); mass spectrum (70eV) m/e 252 (M^+), 251 (M^+-1), 237 (M^+-15), and 85 ($M^+-C_{12}H_{25}$).

Synthesis of 6-Octadecanal.- The triphenylphosphonium salt of the THP ether of hexamethylenechlorohydrin[6] (100 ml of a 0.75 M solution in THF) was injected into a 500 ml 3-neck flask which had been previously flame-dried and purged with nitrogen. The solution was chilled in ice-MeOH, and n-butyllithium (34 ml of 2.2 M in hexane) was injected at such rate as to keep the temperature below 15°. Dodecanal (15 ml, 68 mmoles) was injected. The bath was removed, and the mixture was stirred for 1.5 hr. The mixture was diluted with water and extracted with petroleum ether. The extract was washed with water and dried (Na_2SO_4). The solvent was removed and the crude tetrahydropyranyl ether of 6-octadecen-1-ol was then oxidized by the general procedure above using pyridinium chlorochromate (21.6 g, 100 mmoles) and trifluoroacetic acid (11.4 g, 100 mmoles) in methylene chloride (250 ml). The crude aldehyde could not be distilled without decomposition and was purified by passage through silica gel (150 g) eluting with 400 ml each of 5% and 10% ethyl acetate in hexane. Removal of solvent provided 15.2 g (85%) of the aldehyde: n_D^{21} 1.4567; ir (CCl_4) 2720 (CHO) and 1730 cm^{-1} (C=O); nmr (CCl_4) δ 4.46 (t, 2, $\underline{CH_2}CHO$) 5.26 (broad t, 2, vinyl H), and 9.66 ppm (t, 1, J=1, CHO); mass spectrum (70eV) 266 (M^+), 248 (M^+-H_2O), 328 ($M^+-C_2H_4$), 29 (CHO^+).

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REDUCTION OF 2-FUROIC ACID WITH METAL-AMMONIA SOLUTIONS

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The synthesis of 2,5-dihydrofurans *via* the metal-alcohol-ammonia reduction of furan compounds[1-6] requires a furan ring activated by either carboxyl or phenyl groups. However, product yields in these reactions, are extremely sensitive to reactants and reaction conditions. We have found that addition of 3 equivalents of finely divided lithium to a solution of 2-furoic acid in methanol and dry liquid ammonia affords 2,5-dihydrofuran-2-carboxylic acid in 90% yield. 5-Methyl-2-furoic acid was also reduced under the same conditions to give a 1:1 mixture of *cis* and *trans* diastereoisomers, also in 90% yield.