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A NEW METHOD FOR THE CONVERSION OF ALDEHYDES TO METHYL ESTERS USING PYRIDINIUM DICHROMATE AND METHANOL IN DIMETHYLFORMAMIDE.

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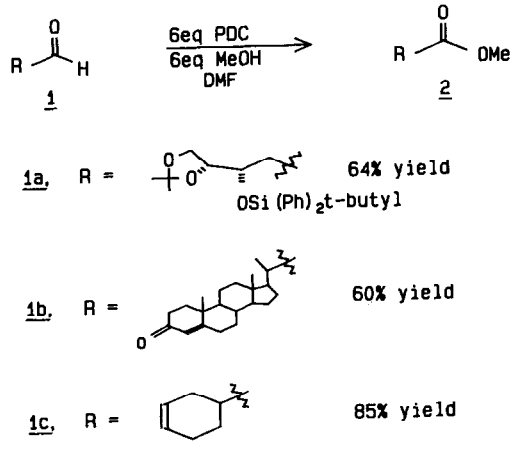
Abstact: A new method for the conversion of aldehydes to methyl esters using pyridinium dichromate and methanol in DMF is described.

Recently Corey and Samuelsson[1] reported the one step conversion of primary alcohols in the carbohydrate series to the corresponding carboxylic tert-butyl esters using the Collins reagent[2], acetic anhydride and tert-butyl alcohol in methylene chloride-dimethylformamide (DMF).

We have found that methyl esters can be formed directly from aldehydes (and to a lesser extent from alcohols) by adding pyridinium dichromate[3] (PDC) to a solution of the aldehyde and methanol in dry DMF. The presence of methanol allows for the formation of the methyl hemiacetal which, when oxidized by PDC, provides the methyl ester. Surprisingly, it appears that the oxidation of methanol by PDC is slow in comparison to the oxidation of the methyl hemiacetal. On a 1 mmol scale, the conversion of decyl aldehyde to methyl decanoate was found to proceed best when 6 mmol of methanol and 6 mmol of PDC were added and the reaction mixture stirred at room temperature for 16 h. Attempts at forming the ethyl ester or isopropyl ester by using ethanol or isopropanol proved less effective, with large amounts of decyl aldehyde remaining unreacted or decanoic acid being formed. In the case of benzaldehyde, since hemiacetal formation occurs slowly in unreactive aromatic aldehydes, we were not surprised to notice that only small quantities of the methyl ester was formed after three days at room temperature .

Attempts at converting decyl alcohol to methyl decanoate, in one pot, proved less effective with considerable amounts of decyl alcohol, decyl aldehyde and decanoic acid present even when PDC was used in a twelve fold excess . This method is compatible with various functional groups as illustrated in scheme I, and methyl esters 2a[4], 2b[4], and 2c[4] are formed in 64%, 60% and 85% yield from the respective aldehydes.

SCHEME I



EXPERIMENTAL

General Procedure

To a solution of decyl aldehyde (156 mg, 1 mmol) in methanol (0.24 mL, 6 mmol) and dry dimethylformamide (5 mL), at room temperature under a nitrogen atmosphere, was added pyridinium dichromate (2.25 g, 6 mmol) and the reaction mixture stirred for 20 h. Comparison with commercially available materials showed the mixture to contain methyl decanoate with traces of decyl aldehyde and decanoic acid (ratio of $RCHO/RCO_2Me/RCO_2H$ was found to be 2/96/2 by g.c.). The solution was poured into hexanes (150 mL)/water (50 mL), filtered over Celite, the water layer extracted with hexanes (3 x 50 mL) and the combined hexanes extracts dried over magnesium sulfate. Removal of the solvent, in vacuo, gave methyl decanoate in 87% yield (identical by g.c. to the commercially available material).

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REFERENCES

1. Corey, E.J.; Samuelsson, B. *J. Org. Chem.* **1984**, 49, 4735.
2. Collins, J.C.; Hess, W.W.; Frank, F.J. *Tetrahedron Lett.* **1968**, 3363.
3. Corey, E.J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.
4. Satisfactory ^1H NMR(200 MHz) and mass spectral data were obtained for compounds 2a, 2b and 2c.

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