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CHLOROTRIMETHYLSILANE CATALYSED ACYLATION OF ALCOHOLS¹

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Abstract: *A variety of alcohols are converted into the corresponding acetates upon treatment with acetic anhydride and catalytic amount of chlorotrimethylsilane in acetonitrile (or dichloromethane).*

The acylation of alcohols is one of the most frequently employed reactions in organic synthesis² which is normally carried out using acetic anhydride or acetyl chloride and a base such as pyridine or triethylamine. The rate of acylations is known to be raised multifold if 4-dimethylaminopyridine (DMAP)^{2b} is used as a co-catalyst. However since the medium of these reactions is basic, sometimes base sensitive substrates lead to the decreased yields of the desired acetates. In view of this, recently Vedjes et al.³ have introduced tributylphosphine as an excellent catalyst for acylation of alcohols. Owing to its reduced basicity compared to DMAP it has certain advantages. In addition to this a few other

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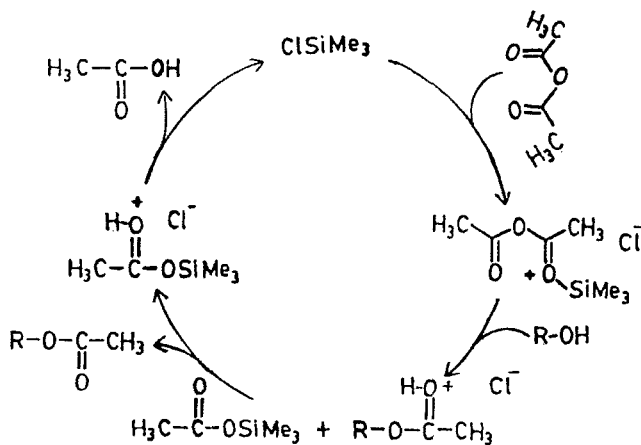






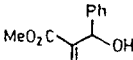
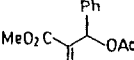
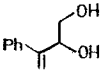
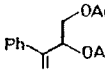





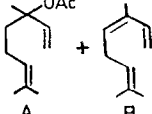




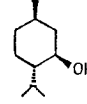
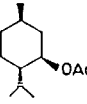




FIGURE 1

catalysts such as CoCl_2^4 and most recently scandium triflate⁵ have been introduced as mildly acidic catalysts for acylation of alcohols.

Although scandium triflate appears to be the best catalyst so far, we have found that chlorotrimethylsilane (CTMS) effectively catalyses acylation of a variety of alcohols in excellent yields. The proposed catalytic cycle for this reaction is represented in Figure 1. The reaction works well with primary, secondary and allylic alcohols (cf. Table 1), however, elimination is observed with tertiary alcohols (cf. entries 6 and 7 in Table 1). On the other hand at lower temperatures ($-20\text{ }^\circ\text{C}$ to $0\text{ }^\circ\text{C}$) the tertiary alcohols were found unreactive. Further, all the optically active alcohols (cf. entries 11, 13, 14, 15 and 16), as expected, gave the corresponding acetates with retention of configurations. After screening various solvents for this reaction it was observed that the reactions gave better

Table - 1
Chlorotrimethylsilane catalysed acylation of alcohols.

| Entry | Alcohols | Acetates | Via Method "A" | | Via Method "B" | |
|-------|---|---|-----------------|-----------|------------------|-----------|
| | | | Yield (%) | Time (hr) | Yield (%) | Time (hr) |
| 1 |  |  | 90 | 2 | 96 | 2 |
| 2 |  |  | 89 | 3 | 91 | 2 |
| 3 |  |  | 94 | 3 | - | - |
| 4 |  |  | 84 | 5 | 90 | 4 |
| 5 |  |  | 78 | 4 | - | - |
| 6 |  |  | 78 | 3 | 80 | 3 |
| 7 |  |  | 82 | 3 | - | - |
| 8 |  |  | A = 5 B = 70 | 24 | A = 13 B = 76 | 24 |
| 9 |  |  | 93 | 2 | 95 | 2 |
| 10 |  |  | 91 | 2 | 91 | 2 |
| 11 |  |  | 86 | 2 | 96 | 2 |
| 12 |  |  | 95 | 2 | 95 | 2 |

(continued)

Table 1 Continued

| | | | | | | |
|----|--|---------------------------|----|---|----|---|
| 13 | | | 72 | 4 | 74 | 3 |
| 14 | | | 78 | 3 | 80 | 3 |
| 15 | | | 69 | 4 | 73 | 4 |
| | | $\alpha : \beta = 40, 60$ | | | | |
| 16 | | | 81 | 4 | 84 | 4 |
| | | $\alpha : \beta = 40, 60$ | | | | |

Method "A" - Dichloromethane was used as solvent.

Method "B" - Acetonitrile was used as solvent.

yields in dichloromethane than in acetonitrile (cf. Table 1). However, for the acylation of D-glucose, acetic anhydride was used as solvent. In view of the commercial availability of CTMS and mild (ambient temperature) reaction conditions this method of acylation appears to be useful.

General experimental procedure: To a stirred mixture of acetic anhydride (4 mmol) and an alcohol (2 mmol) in acetonitrile or dichloromethane (4 ml) was added CTMS (0.1 mmol) dissolved in 1 ml of the solvent. The reaction mixture was stirred for the time indicated in Table 1. After the reaction was complete, the solvent was removed under vacuum and the crude product purified by column chromatography to obtain the pure acetate.

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