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Montmorillonite Clay Catalysis V[1]: An Efficient and Facile Procedure for Deprotection of 1,1-Diacetates

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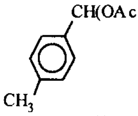
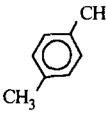
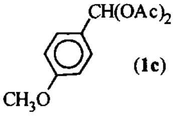
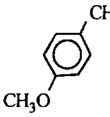
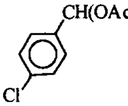
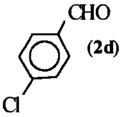
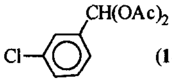
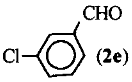
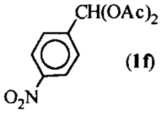
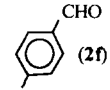
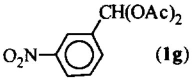
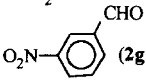
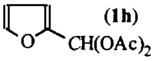
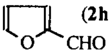
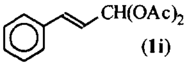
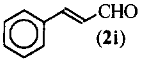
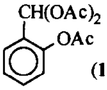
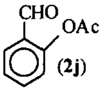
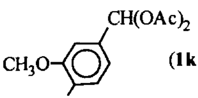
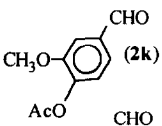
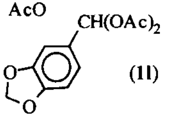
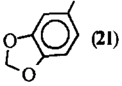
Abstract: A variety of 1,1-diacetates are easily deprotected in good to excellent yield under catalysis by montmorillonite clays in refluxing dichloromethane or benzene. © 1997 Elsevier Science Ltd.

Selective protection and deprotection of functional groups are of great importance in synthetic organic chemistry. In the course of the last decade, 1,1-diacetates have been received increasing attention, since these compounds are stable[2] and easily prepared[1-7] and can serve as an alternative to acetals for the protection of aldehydes[8] and as starting materials for the Diels-Alder cycloaddition reactions.[9-10]

Recently, a number of methods have been developed for conversion of 1,1-diacetates to the corresponding aldehydes. To our knowledge, the following methods have been used: a) alcoholic sulfuric[11] or hydrochloric[12] acid, b) either sodium hydroxide or potassium carbonate in aqueous THF overnight,[2] c) boron triiodide-*N,N*-diethylaniline complex,[13] d) ceric ammonium nitrate (CAN) coated on silica gel in dichloromethane,[14] e) neutral alumina under microwave irradiation,[15] f) potassium phenoxides,[16] and g) montmorillonite K 10[17] or KSF[18] under microwave irradiation. Each of the above methods has its own merit and some drawbacks. Method a) requires the use of a strong acids in which other functional groups in the molecule may not tolerate; method b) needs long reaction time and no detailed results are given; method c) provides low yield (<66%); and methods e) and g) require the use of an additional microwave oven. So far, montmorillonite clay is used for only one compound and no general study is available.

Montmorillionite clays have been extensively used as efficient catalysts for a variety of organic reactions.[19] Recently we have developed an efficient and convenient procedure for preparation of 1,1-diacetates from aldehydes under catalysis of montomorillonite clays.[1] However, the deprotection of 1,1-diacetates directly using conventional laboratory equipment catalysed by montmorillonite clays remains unreported. In connection with our work on montmorillonite clays catalysis,[20] we now describe an efficient deprotection of 1,1-diacetates under catalysis of montmorillonite K 10 and KSF in refluxing dichloromethane or benzene.

Table 1. Deprotection of 1,1-Diacetates Catalysed by Montmorillonite Clays

Entry	Substrate	Product	Catalyst	Solvent	Time(min)	Yield(%)[a]
1	$C_6H_5CH(OAc)_2$ **(1a)**	C_6H_5CHO **(2a)**	K10	CH_2Cl_2	20	98
			KSF	CH_2Cl_2	20	96
2	 **(1b)**	 **(2b)**	K10	CH_2Cl_2	20	99
			KSF	CH_2Cl_2	30	98
3	 **(1c)**	 **(2c)**	K10	CH_2Cl_2	15	98
			KSF	CH_2Cl_2	20	96
4	 **(1d)**	 **(2d)**	K10	CH_2Cl_2	20	98
			KSF	CH_2Cl_2	30	96
5	 **(1e)**	 **(2e)**	K10	CH_2Cl_2	30	95
			KSF	CH_2Cl_2	40	93
6	 **(1f)**	 **(2f)**	K 10	C_6H_6	20	98
			KSF	C_6H_6	20	98
7	 **(1g)**	 **(2g)**	K 10	C_6H_6	20	98
			KSF	C_6H_6	25	95
8	 **(1h)**	 **(2h)**	K10	CH_2Cl_2	20	98
			KSF	CH_2Cl_2	25	96
9	 **(1i)**	 **(2i)**	K10	CH_2Cl_2	45	98
			KSF	CH_2Cl_2	50	96
10	 **(1j)**	 **(2j)**	K10	CH_2Cl_2	30	88
			KSF	CH_2Cl_2	35	86
11	 **(1k)**	 **(2k)**	K10	CH_2Cl_2	30	95
			KSF	CH_2Cl_2	30	93
12	 **(1l)**	 **(2l)**	K10	CH_2Cl_2	20	98
			KSF	CH_2Cl_2	25	97

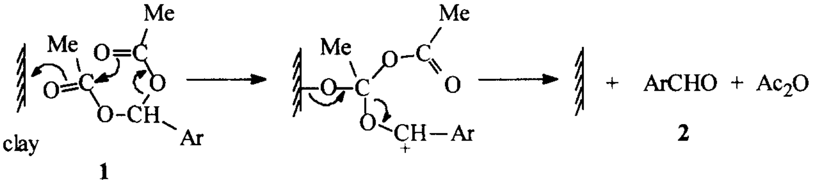
[a] Isolated yield.

When 1,1-diacetates (**1**) are heated in refluxing dichloromethane or benzene in the presence of montmorillonite K 10 or KSF, the corresponding aldehydes (**2**) are obtained in good to excellent yield (Table 1). No additional water is needed for the reaction. K 10 and KSF give similar results in terms of reaction time and yield. (*p*-Nitrophenyl)methanediol diacetate (**1f**) and (*m*-nitrophenyl)methanediol diacetate (**1g**) provide poor conversion rate (<50%) in refluxing dichloromethane for 4 h whereas 95~98% cleavage yield are obtained in refluxing benzene for 20 min, possibly due to the strongly electron-withdrawing nitro substituent which requires a high refluxing temperature. It is pertinent to note that the phenolic acetate function (Entries 10 and 11) remains unaffected under these reaction conditions as well as the acetal moiety in **1l**. We have also tried the reaction of 4-methoxyphenyl acetate and cholesteryl acetate in refluxing dichloromethane for 2 h in the catalysis of K-10 or KSF. However, neither of the substrates gives the hydrolysis products and the materials are recovered quantitatively. Therefore the present procedure is a selective deprotection of aryl aldehyde diacetates to aryl aldehydes in the presence of the phenolic acetate and alcoholic acetate.

It is noteworthy that the reaction takes longer time at room temperature, for example, complete conversion of (4-methylphenyl)methanediol diacetate (**1b**) and (3,4-methylenedioxyphenyl)methanediol diacetate (**1l**) to the corresponding aldehydes (**2b** and **2l**) need 6 h in dichloromethane under catalysis of montmorillonite K 10.

Although the mechanism of the hydrolysis of aryl aldehyde diacetates in aqueous hydrochloric acid was studied,[21] the mechanism of this reaction is different. The hydroxamate test identify the presence of acetic anhydride in the reaction products. Furthermore, neither additional water nor anhydrous conditions affect the reaction rate. These results show that the reaction undergoes a unimolecular decomposition of 1,1-diacetates to give an aldehyde and acetic anhydride in which the clays, we suppose, play a Lewis acid role (Scheme 1).

Scheme 1



In summary, we have developed a rapid, selective, simple, inexpensive, and efficient procedure for deprotection of 1,1-diacetates, which uses conventional laboratory equipment and does not require an aqueous workup.

General procedure for deprotection of 1,1-diacetates:

A mixture of 1,1-diacetates (prepared according to our previous method[1]) (**1**, 2.00 mmol), dichloromethane or benzene (3 ml) and montmorillonite K 10 or KSF (50 mg) was stirred at refluxing temperature for the length of time indicated in Table 1. The reaction was monitored by TLC. After cooling, the mixture was chromatographed on silica gel (petroleum-dichloromethane as eluent) to give the corresponding aldehydes (**2**) in the yield of 86-99% (Table 1). The products were confirmed by ^{1}H NMR and by comparison of their R_F values on TLC and m.p. or b.p. with authentic samples.

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