J. Chem. Research (S), 1998, 382–383†

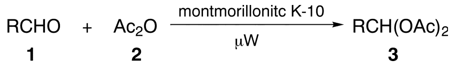
Facile Synthesis of 1,1-Diacetates from Aldehydes Using Montmorillonite K-10 Clay under Microwave Irradiation†

Dipankar Karmakar, Dipak Prajapati and Jagir S. Sandhu*

Regional Research Laboratory, Jorhat-785 006, Assam, India

Selective and easy synthesis of acylals in dry media using montmorillonite K-10 clay in an Erlenmeyer flask under microwave activation in remarkably reduced reaction time is described.

Acylals or diacetates are synthetically useful as aldehyde protecting groups[1] as alternatives to acetals and are important building blocks for the synthesis of dienes for Diels–Alder cycloaddition reactions.[2] Usually the formation of 1,1-diacetates is catalysed by strong acids[3] such as sulfuric, phosphoric or methanesulfonic, or by Lewis acids such as $ZnCl_2$[4] and $FeCl_3$.[5] These methods[6] have not been entirely satisfactory, owing to such drawbacks as low yields, long reaction time, corrosiveness and effluent pollution. Olah Mehrotra[7] reported the use of Nafion-II as a catalyst where the yields of products are moderate and reaction times are generally 3–5 h. Phosphorus(II) chloride[8] and β-zeolite[9] have also been employed for this conversion.[10] However, in most cases either a long reaction time (up to 120 h in the case of 2-furfuraldehyde with PCl_3[8]) or a low yield of product (4% in the case of *p*-nitrobenzaldehyde[7]) is observed. Therefore, there is merit in developing a truly catalytic process using inexpensive and non-polluting reagents. Herein we disclose the first example that montmorillonite K-10 clay can be utilized for the formation of acylals from aldehydes using microwave irradiation[11] under solvent-free conditions[12] in almost quantitative yields. The reaction proceeds efficiently at ambient pressure within minutes, in the absence of solvent conditions[12] in almost quantitative yields. The reaction proceeds efficiently at ambient pressure within minutes, in the absence of solvent.



$$\underset{\mathbf{1}}{RCHO} + \underset{\mathbf{2}}{Ac_2O} \xrightarrow[\mu W]{\text{montmorillonitc K-10}} \underset{\mathbf{3}}{RCH(OAc)_2}$$

Scheme 1

In a typical case, *p*-chlorobenzaldehyde (10 mmol), acetic anhydride (20 mmol) and montmorillonite K-10 clay (0.3 g) were mixed without solvent in an Erlenmeyer flask, placed in a commercial microwave oven and irradiated for 5 min. The mixture was allowed to reach room temperature and after completion of reaction the corresponding *p*-chlorobenzylidienic diacetate, mp 80–81 °C (lit.,[8] 80–81 °C) was obtained in 98% yield. Similarly, other aldehydes gave the corresponding 1,1-diacetates in good purity. The excellent yields demonstrate the efficiency of the montmorillonite K-10 clay catalyst (Table 1). It is remarkable that *p*-nitrobenzaldehyde and cinnamaldehyde, gave 85–90% yields, in contrast to yields of 4 and 30% respectively in an earlier report.[7] Also worthy of mention in our case is that α,β-unsaturated aldehydes (entries 7,8) gave no isomerization of double bonds under the reaction conditions. The reverse reaction, *i.e.* selective deprotection of the diacetates to give aldehydes, has been reported[13] to occur under microwave irradiation using a neutral alumina surface as catalyst, while montmorillonite K-10 induces the formation of 1,1-diacetates under microwave irradiation in excellent yields. The generality of this acylal-forming reaction was tested by subjecting polycyclic aromatic aldehydes to similar conditions. The aldehydes examined were 2-naphthaldehyde and 9-phenanthraldehyde, which yielded the corresponding 1,1-diacetates in 78 and 75% respectively (Table 1).

In conclusion, the present new method for the formation of acylals, without any solvent under microwave irradiation, offers significant improvements over the existing procedures and constitutes a useful and important addition to the present methodologies. The main advantages are mild reaction conditions, reduced reaction time, lack of side-products and excellent yields.

Table 1 1,1-Diacetates from aldehydes using montmorillonite K-10 under microwave activation

Entry	Substrate[a]	Yield[b] (%)	Yield reported (%)	Reaction time/min	Reaction time reported/h
1	*p*-Chlorobenzaldehyde	98	888	6	48
2	*m*-Chlorobenzaldehyde	90	86.53	7	0.75
3	*p*-Methoxybenzaldehyde	95	928	8	12
4	*p*-Nitrobenzaldehyde	85	48	10	24
5	*p*-Tolualdehyde	85	808	8	6
6	Benzaldehyde	96	988	10	12
7	Cinnamaldehyde	90	308	15	24
8	Crotonaldehyde	82	758	12	43
9	2-Furfuraldehyde	80	708	15	120
10	Isobutyraldehyde	90	908	10	2.5
11	2-Naphthaldehyde	78	676[c]	15	24
12	9-Phenanthraldehyde	75	586[c]	20	168

[a]Products were identified by the comparison of IR, NMR spectra and melting points with those of authentic samples. [b]Refers to the yield of pure isolated products.

---

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Experimental

Mps were taken in open capillary tubes on a Buchi apparatus and were uncorrected. IR spectra were recorded as KBr discs on a Perkin-Elmer 237B IR spectrometer. Microanalyses were performed on a Perkin-Elmer 240C analyser. The ^{1}H NMR spectra were recorded on a Varian T-60 machine using tetramethylsilane (TMS) as the internal standard. The chemical shifts are recorded as δ values. The montmorillonite K-10 was of commercial grade from Aldrich Chemical Company. All other chemicals were purified by distillation or crystallization prior to use.

General Procedure for the Preparation of 1,1-*Diacetates in the Absence of Solvent under Microwave Irradiation.*—A mixture of *p*-chlorobenzaldehyde (1.41 g, 10 mmol), acetic anhydride (2.04 g, 20 mmol) and montmorillonite K-10 clay (0.3 g) in an Erlenmeyer flask at room temperature was placed in a commercial microwave oven (operating at 2450 MHz frequency) and irradiated for 5 min. Upon completion, the reaction mixture was allowed to reach room temperature (monitored *via* TLC), water was added and the K-10 clay was filtered off. The catalyst was washed with dichloromethane (2 × 20 ml) and then the filtrate was extracted with dichloromethane (3 × 20 ml). The combined extract was washed with 10% HCl solution (20 ml) and brine (2 × 20 ml) dried over anhydrous sodium sulfate and distilled. The *p*-chlorobenzylidene diacetate thus obtained was purified by column chromatography using dichloromethane-light petroleum (1:1) as the eluent, mp 80–81 °C (lit.,[8] 80–81 °C) (Table 1). Similarly other aldehydes gave the corresponding 1,1-diacetates (entries, 2 to 12) in 75–96% yields. All the products were characterized by infrared and ^{1}H NMR spectroscopy and finally by comparison with authentic samples.

Received, 25th February 1998; Accepted, 12th March 1998
Paper E/8/01594E

References

1 S. V. Liebermann and R. Connor, *Org. Synth.*, 1995, **Coll. Vol. III**, 441; T. W. Greene, *Protective Groups in Organic Synthesis*, 1st edn., Wiley, New York, 1981, p. 116.

2 B. B. Snider and S. G. Amin, *Synth. Commun.*, 1978, **8**, 117; G. Saucy, R. Marbet, H. Lindlar and O. Isler, *Helv. Chim. Acta*, 1959, **42**, 1945.

3 I. Freeman and E. M. Karchefski, *J. Chem. Eng. Data*, 1977, **22**, 355; M. J. Gregory, *J. Chem. Soc. B*, 1970, 1201.

4 I. Seriabine, *Bull. Soc. Chim. Fr.*, 1961, 1194; F. O. Cockerille, *U.S. Pat.*, 2 264 789, 1941 (*Chem. Abstr.*, 1942, **36**, 1620).

5 K. S. Kochhar, B. S. Bal, R. P. Deshpande, S. N. Rajadhyaksha and H. W. Pinnick, *J. Org. Chem.*, 1983, **48**, 1765.

6 (*a*) N. Deka, D. J. Kalita, R. Borah and J. C. Sarma, *J. Org. Chem.*, 1997, **62**, 1563; (*b*) E. J. Enholm and H. Satici, *Tetrahedron Lett.*, 1991, **32**, 2433; (*c*) A. J. Fry, A. K. Rho, L. R. Sherman and C. S. Sherwin, *J. Org. Chem.*, 1991, **56**, 3283.

7 G. A. Olah and A. K. Mehrotra, *Synthesis*, 1982, **962**.

8 J. K. Michie and J. A. Miller, *Synthesis*, 1981, **824**.

9 C. Pereira, B. Gigante, M. J. Marcelo-Curto, H. Carreyre, G. Perot and M. Guisnet, *Synthesis*, 1995, 1077; P. Kumar, V. R. Hedge and T. P. Kumar, *Tetrahedron Lett.*, 1995, **36**, 601.

10 M. V. Joshi, C. S. Narashimhan and D. Mukesh, *Zeolites*, 1995, **15**, 597; M. V. Joshi and C. S. Narasimhan, *Indian J. Catal.*, 1993, **141**, 308; B. P. Bandgar, N. P. Mahajan, D. P. Mulay, J. L. Thote and P. P. Wadgaonkar, *J. Chem. Res.* (*S*), 1995, 470.

11 S. Caddick, *Tetrahedron*, 1995, **51**, 10403; D. M. Mingos and D. R. Baghurst, *Chem. Soc. Rev.*, 1991, **20**, 1; R. J. Giguere, in *Organic Synthesis: Theory and Application*, JAI Press, 1989, vol. 1, pp. 103–172.

12 V. Vu Muc Thuoy and P. Maitte, *Bull. Soc. Chim. Fr.*, 1979, **11**, 264; D. Villenin, B. Labiad and M. Hammadi, *J. Chem. Soc., Chem. Commun.*, 1992, 1192; E. Gutierrez, A. Loupy, G. Bram and E. Ruiz-Hitzky, *Tetrahedron Lett.*, 1989, **30**, 945; M. Csiba, M. Cleophax, A. Loupy, J. Malthete and S. D. Gero, *Tetrahedron Lett.*, 1993, **34**, 1787.

13 R. S. Varma, A. K. Chatterjee and M. Varma, *Tetrahedron Lett.*, 1993, **34**, 3207.