Monatshefte für Chemie 131, 417–420 (2000)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Microwave Induced Synthesis of Geminal Diacetates from Aldehydes Using Envirocat EPZ10® Without Solvent

Babasaheb P. Bandgar*, **Sangita S. Makone,** and **Sulakshana R. Kulkarni**

School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded-431606, India

Summary. A simple, efficient, and environmentally friendly synthesis of geminal diacetates using Envirocat EPZ10® under microwave activation and solvent-free conditions is described. Easy separation and recyclability of the catalyst, high reaction rates, high yields, and easy work-up are important advantages of this method.

Keywords. Envirocats: Microwaves: Aldehydes; Geminal diacetates.

Introduction

Geminal or 1,1-diacetates are synthetically useful as aldehyde protecting groups [1] as alternatives to acetals. These diacetates are stable towards aqueous acids and mild bases [2] and are useful as important building blocks for the synthesis of dienes for *Diels-Alder* cycloaddition reactions [3]. Diacetates of some aldehydes are reported to be good cross-linking reagents for cellulose in cotton [4] and activators in the composition of a bleaching mixture for wine stained fabric [5]. A patent claims the utility of 1,1-diacetates as protecting groups in the synthesis of an intermediate for chrysanthemic acid [6].

Usually, the formation of 1,1-diacetates is catalyzed by protic acids [7] such as sulfuric, methanesulfonic, or phosphoric acid, by *Lewis* acids, *e.g.* $FeCl_3$ [2], PCl_3 [8], BF_3 [9], $ZnCl_2$ [10], *etc.* and by the super acid Nafion-H [11]. More recently, Me_3SiCl-NaI [12], I_2 [13], sulfated zirconia [14], and zeolites [15] of different types have also been used as catalysts for this conversion. However, the application of conventional protic or *Lewis* acid catalysts entail the problems of corrosivity, tedious work-up, and effluent pollution. In some cases, either low yield of product or long reaction times have been observed [8]. Therefore, the development of new reagents providing higher efficiency, better yields, environmentally more friendly procedures, high reaction rates, and easy work-up is of more interest.

---

* Corresponding author

There has been a considerable growth in interest in recent years in the catalysis of organic reactions by inorganic reagents supported on high surface area inorganic materials [16]. Envirocats®, a new family of supported reagents, constitute a significant breakthrough in environmentally friendly chemistry. These reagents, non-toxic powders which can be filtered off easily and may be reused after activation, are capable of catalyzing various reactions [17]. Envirocat EPZ10® exhibits both *Brønsted* and *Lewis* acid characteristics [17]. We report herein the first example of Envirocat EPZ10® applied for the synthesis of 1,1-diacetates under solvent-free conditions using microwave irradiation.

Results and Discussion

The results of the reaction geminal diacetates (cf. Scheme) are summarized in Table 1. When aldehydes were mixed with Envirocat EPZ10® and Ac_2O and exposed to microwaves, the corresponding diacetates were obtained in excellent yields and high purity. The reaction worked equally well for a dialdehyde (entry 13) The efficiency of Envirocat EPZ10® can be clearly visualized in the case of aromatic aldehydes with an electron withdrawing group where the corresponding diacetates have been obtained in excellent yields (entries 8–11), whereas *e.g.* the phosphorus trichloride catalyzed reaction gave poor yields in this case and required a very long reaction time (120 h) [8].

$$R\mathrm{CHO} + \mathrm{Ac_2O} \xrightarrow[\mathrm{MW}]{\text{Envirocat EPZ10}^{\circledR}} R\mathrm{CH(OAc)_2}$$

Scheme

In conclusion, Envirocat EPZ10® has been found to be a convenient and very effective heterogenous catalyst for the synthesis of 1,1-diacetates from a variety of aldehydes under microwave irradiation and solvent-free conditions. The reaction is quite general. The obivious advantages of this methodology are easy separation and recyclability of the catalyst, high reaction rates, high yields, easy work-up, and an eco-friendly procedure.

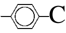
Experimental

Envirocat EPZ10® was obtained from Contract Chemicals, England, and used without activation. Commercially available aldehydes were used as obtained. IR spectra were recorded on a Bomem MB 104 FT-IR spectrometer and ^1H NMR spectra on a Perkin-Elmer 90 MHz spectrometer using *TMS* as an internal standard.

General Procedure

A mixture of the aldehyde (5 mmol), acetic anhydride (10 mmol for monoaldehyde or 20 mmol for dialdehyde) and Envirocat EPZ10® (100 mg) was irradiated with microwaves for the specified time (Table 1). After completion of the reaction (TLC), diethyl ether ($2 \times 10\,cm^3$) was added to the reaction mixture, and EPZ10® was filtered off. After drying (Na_2SO_4), the ether was evaporated under reduced pressure to give the products in high yield and in almost pure form.

Table 1. Microwave induced EPZ10® catalyzed synthesis of geminal diacetates

Entry	Aldehyde	Product [7–15]	Reaction time (sec)	Yield[a] (%)
1	Propanal	Propanal-1,1-diacetate	10	89
2	Butyraldehyde	Butyraldehyde-1,1-diacetate	12	85
3	Hexanal	Hexanal-1,1-diacetate	40	87
4	Nonanal	Nonanal-1,1-diacetate	55	89
5	4-Bromobenzaldehyde	4-Bromobenzaldehyde-1,1-diacetate	30	87
6	4-Chlorobenzaldehyde	4-Chlorobenzaldehyde-1,1-diacetate	10	92
7	2,4-Dichlorobenzaldehyde	2,4-Dichlorobenzaldehyde-1,1-diacetate	40	90
8	2-Nitrobenzaldehyde	2-Nitrobenzaldehyde-1,1-diacetate	50	90
9	3-Nitrobenzaldehyde	3-Nitrobenzaldehyde-1,1-diacetate	30	83
10	4-Nitrobenzaldehyde	4-Nitrobenzaldehyde-1,1-diacetate	40	89
11	3-Nitro, 4-chlorobenzaldehyde	3-Nitro-4-chlorobenzaldehyde-1,1-diacetate	20	90
12	3,4,5-Trimethoxybenzaldehyde	3,4,5-Trimethoxybenzaldehyde-1,1-diacetate	30	85
13	OHC––CHO	$(AcO)_2HC$––$CH(OAc)_2$	45	89

[a] Products were characterized by their physical constants [7–15], their spectroscopic characteristics (IR, ^1H NMR), and by comparison with authentic samples; the yields refer to pure isolated products

Acknowledgements

We thank UGC, New Delhi, for financial assistance and Contract Chemicals, England, for a generous gift of Envirocat EPZ10®.

References

[1] Green TW (1991) Protective Groups in Organic synthesis, 2nd edn. Wiley, New York

[2] Kochhar KS, Bal BS, Deshpande RP, Rajadhyksha SR, Pinnick HW (1983) J Org Chem **48**: 1785

[3] Snider BB, Amin SG (1978) Synth Commun **8**: 117; Saucy G, Marber R, Lindlar H, Isler O (1959) Helv Chim Acta **42**: 1925

[4] Frick JG Jr, Harper RJ Jr (1984) J Appl Polym Sci **29**: 1433

[5] Sanderson WR (1984) Eup Pat Appl EP **125**: 781 (Chem Abstr **102**: 64010k)

[6] Kula J (1988) Pol Pat PL **143**: 824 (Chem Abstr **112**: 216290y)

[7] Freeman I, Karchefski EM (1977) J Chem Eng Data **22**: 355; Gregory MJ (1970) J Chem Soc B 1201

[8] Muchie JK, Miller JA (1984) Synthesis 824

[9] March J (1986) Advanced Organic Chemistry, 3rd edn. Wiley Eastern, New Delhi, p 861

[10] Scriabine I (1961) Bull Soc Chim Fr 1194

[11] Olah G, Mehrotra AK (1982) Synthesis 962

[12] Daka N, Borah R, Kalita DJ, Sarma JC (1998) J Chem Res (S) 94
[13] Daka N, Kalita DJ, Borah R, Sarma JC (1997) J Org Chem **62**: 1563
[14] Raju SVN (1996) J Chem Res 68
[15] Pereira CB, Gigante MJ, Marcelo-Curto H, Carreyre G, Perot, Guisnet M (1995) Synthesis 1077; Kumar P, Hegde VR, Kumar TP (1995) Tetrahedron Lett **36**: 601 Joshi MV, Narasimhan CS (1993) J Catalysis **141**: 308
[16] Contract Chemicals (1994) Envirocats-Supported Reagents: Product Information. Merseyside L34 9HY, England
[17] Bandgar BP, Zirange MB, Wadgaonkar PP (1996) Synlett **2**: 149; Bandgar BP, Hajare CT, Wadgaonkar PP (1995) J Chem Res (S) **1**: 90; Bandgar BP, Sadavarte VS (1999) Synth Commun **29**: 2587

Received November 3, 1999. Accepted November 24, 1999

Verleger: Springer-Verlag KG, Sachsenplatz 4–6, A-1201 Wien. – Herausgeber: Österreichische Akademie der Wissenschaften, Dr.-Ignaz-Seipel-Platz 2, A-1010 Wien, und Gesellschaft Österreichischer Chemiker, Eschenbachgasse 9, A-1010 Wien. – Redaktion: Währinger Straße 38, A-1090 Wien. – Satz und Umbruch: Thomson Press Ltd., New Delhi, India. – Offsetdruck: Eugen Ketterl Gesellschaft m.b.H., Kreuzbrunn 19, A-3001 Mauerbach. – Verlagsort: Wien. – Herstellungsort: Mauerbach.– Printed in Austria.