Ultrasound and microwave activated preparation of ZrO_2-pillared clay composite: catalytic activity for selective, solventless acylation of 1,*n*-diols

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Abstract

We herein report for the first time, a new and efficient method using ultrasonic activation for intercalation by ion exchange and microwave heating for formation of zirconium polyoxycationic species in the preparation of ZrO_2-pillared clay composite with improved physico-chemical properties and significant reduction in processing time. Acetic anhydride under solventless conditions with microwave irradiation in the presence of ZrO_2-pillared clay was used for the mono-acylation of diols and alcohols in very good yield.
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1. Introduction

Hydroxy zirconium compounds have been used to form stable oxide pillars between the silicate layers of smectite clays [1]. These pillared interlayer clays have many of the characteristics of two-dimensional zeolite-like materials. They are prepared by exchanging charge compensating cations between the clay layers with oligomeric polyoxometal cations formed by hydrolysis of metal salts, [2] which on heating form stable metal oxide clusters acting as pillars, resulting in the separation of interlayer space of molecular dimensions [3]. This propping apart of the clay sheets imparts high surface area, increased acidity besides size and shape selectivity as compared to the small channels in zeolites. Such pillared clays with relatively large channels provide a precisely defined, but flexible, microenvironment for the catalytic reactions. These materials have potential application as catalysts for cracking, selective formation of C_2–C_4 olefins from methanol or CO/H_2 and a wide variety of proton-catalysed reactions [4].

The commercial application of various modified clays, particularly the pillared clays as potential catalysts is hindered by lengthy preparation time and due to their thermal instability. Several methods are reported in literature for the preparation of ZrO_2-pillared clay (Zr-PILC) by varying the zirconium precursor, nature of clays, processing time and drying temperature [5]. The fine tuning of physico-chemical properties of ZrO_2-pillared clay largely depends on the method of preparation [6]. In the present work, we report a novel method using ultrasound and microwave techniques together for the rapid preparation of ZrO_2-pillared clay with microporous solid structure having good thermal and structural rigidity, porosity, enhanced surface area and good catalytic properties.

Ultrasonic irradiation of a liquid results in the phenomena of "acoustic cavitation" that involves the formation, growth and collapse of bubbles in the liquid medium. This violent collapse of bubbles generates high temperatures (several thousands of degrees) and high pressures (hundreds of atmospheres) together with a shock wave [7]. This combined effect enhances the diffusion of zirconium polyoxycationic oligomeric species into the interlayer spacing in the layered structure of montmorillonite clay, also referred to as "microstreaming effect" [8] which facilitates the rapid intercalation process.

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The zirconium polyoxycationic oligomeric pillaring species are prepared by either ageing or refluxing the zirconium oxychloride solution over different intervals of time [9]. The uniform and rapid heating effect of microwaves is well documented in literature [10]. We have investigated the preparation of zirconium polyoxycationic oligomeric pillaring species by microwave heating zirconium oxychloride solution over different intervals of time and compared with the sample prepared by refluxing for 24 h.

Bifunctional reagents are important synthons for organic chemists. Many of these bifunctional reagents utilise 1,n-diols as starting substrates. Chemically non-equivalent hydroxyl groups such as primary, secondary and tertiary ones can be easily differentiated from each other by employing common protection and deprotection strategies. Two chemically equivalent hydroxyl groups such as in 1,n-diols are often difficult to differentiate. Although there are few methods known and various types of catalysts available, this problem still constitutes an active area of research and poses a challenge for developing an efficient methodology [11].

Derivatization of these diols with a stoichiometric amount of reagent usually generates mixture of the unreacted, mono-derivatized and the di-derivatized diols in a statistical distribution of 1:2:1. This statistical distribution can be altered by employing a large excess of the starting diols relative to the protecting reagents thus reducing the amount of bis-protected diols formed. However, separation of the desired product from the excess diols can be problematic. In recent years, several methodologies centred on alleviating these problems for the mono-protection of diols by using stoichiometric amount of sodium hydride/*tert*-butyldimethylsilyl chloride in tetrahydrofuran, [12] acetic anhydride, [13] acetic acid [14] under acidic conditions, acetyl chloride [15] under basic conditions, besides employing alumina, [16] ion exchange resin, [17] phase transfer catalysts [18] and inorganic polymer supports [19], have been reported in literature. All these procedures require careful manipulation, longer reaction time, expensive reagents, different solvents and at different reaction temperatures.

Environmental problems have led to an increased interest in the study of heterogeneous reactions that involve solid reagents supported on high surface area inorganic materials [20]. Keeping in mind the environmental factors there is a need to carry out reactions under solventless conditions and several of them are reported in literature [21]. The advantageous use of the rapid heating effect of microwave induced organic synthesis in the presence of solid support is well documented [22,23]. Microwave irradiation with solid or mineral supports under solvent free condition provides clean chemical processes and is eco-friendly with several advantages over the conventional solution phase reactions such as enhanced reaction rates, higher yields, selectivity and elimination of pollutant organic solvents [24]. Zr-PILC catalyst has the advantage of easy removal, merely by simple filtration.

In continuation of our program to use ultrasound [25] and microwave [26] techniques for heterogeneous catalysed reactions under solventless conditions, we herein report an eco-friendly, efficient and economical method for the preparation of catalyst as well as its application to mono-acylation of 1,n-diols.

2. Experimental

2.1. Preparation of the catalyst

Na^+-montmorillonite with cation exchange capacity of (120 meq./100 g clay) was used as such in all the experiments. $ZrOCl_2 \cdot 8H_2O$ was used as a source for zirconium polyoxocationic species. The 150 ml aqueous solution of $ZrOCl_2 \cdot 8H_2O$ (0.1 M) was taken in a glass beaker and irradiated in a microwave oven for time varying from 5, 10, 20 and 30 min to get the zirconium polyoxycationic species. The best pillaring species was obtained by heating for 10 min at a power level of 640 W. This prepared solution was then added dropwise to the aqueous suspension of 2 wt.% by clay, i.e. 1.5 gm of Na^+-montmorillonite clay in 75 ml water. The mixture was then subjected to sonication for different time (5, 10, 20, 30 and 40 min) for enhancing the pillaring process. The optimum time for sonication was found to be 20 min. The slurry was filtered and washed repeatedly with deionised water till the filtrate was free from chlorides (tested by $AgNO_3$) and dried in air. Samples were then calcined at different temperatures of 120, 550 and 750 °C for 4 h in air to check the thermal stability. The final samples are denoted as MNT (parent clay), PILMNT-24R (prepared by refluxing) and PILMNT-MW10-US20 (prepared by microwave and ultrasonic activation).

2.2. Characterisation of the catalyst

The ZrO_2-pillared clay was characterised by using XRD, BET, XRF analysis to determine the structure and thermal stability, surface area and Zr-content, respectively.

The basal spacing of MNT, PILMNT-24R and PILMNT-MW10-US20 determined from X-ray diffraction analysis of the d_{001} spacing values for the layered structures (XRD, Rigaku D-Max IIIC using Ni-filtered Cu Kα radiation) were found to be 12.9, 21.0 and 22.1 Å, respectively, indicating a substantial expansion of the interlayers due to inclusion of ZrO_2 pillars in the interlamellar space as shown in Fig. 1.

Calcination of MNT, PILMNT-24R and PILMNT-MW10-US20 at 550 °C leads to d_{001} basal spacing values of 7.0, 19.7 and 21.0 Å, respectively. The parent clay is thermally unstable due to weak electrostatic forces existing between the layered structures. However, due to the structural rigidity imparted by pillaring the PILMNT-24R and PILMNT-MW10-US20 samples, they showed a small decrease in basal spacing and are thermally stable. However, on heating to 750 °C, the structure collapsed. Fig. 2
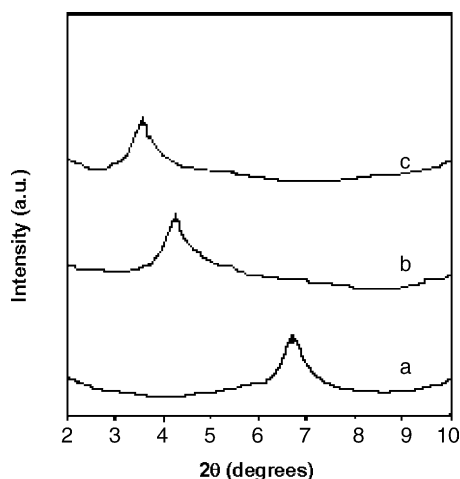
Fig. 1. XRD patterns of (a) MNT (parent clay), (b) PILMNT-24R and (c) PILMNT-MW10-US20.

illustrates the thermal stability of the catalysts before and after calcination.

The percentage weight losses of MNT, PILMNT-24R and PILMNT-MW10-US20 after heating at 550 °C for 4 h were found to be 12.1, 22.2 and 24.1% (by weight), respectively. This is due to the loss of a variety of structural water molecules by dehydration and dehydroxylation resulting in the formation of nano-sized stable metal-oxide pillars in the pillared clays. The observed XRD peaks were broadened on intercalation as a result of the formation of nano-sized crystalline particles. The crystallite sizes calcu-

lated from d_{001} diffraction peak for MNT, PILMNT-24R and PILMNT-MW10-US20 using the Scherrer equation were 17.3, 13.8 and 8.7 nm, respectively.

The Zr-content in MNT, PILMNT-24R and PILMNT-MW10-US20 determined by XRF technique was found to be 0, 15.5 and 16.4% (by mass), respectively.

Fig. 3 shows the nitrogen adsorption–desorption isotherms of MNT, PILMNT-24R and PILMNT-MW10-US20 at 77 K evaluated using adsorption analyser. PILMNT-24R and PILMNT-MW10-US20 showed high initial adsorption at low relative pressure with nearly horizontal plateau up to a relative pressure of ∼0.9, being characteristic of microporous solids. PILMNT-24R and PILMNT-MW10-US20 showed much larger nitrogen adsorption capacity. The hysteresis loop of these materials is H3 type (Fig. 3) according to IUPAC classification [27] with adsorption isotherms of Type I, which is attributed to the slit shaped pores with spacing between the parallel plates. The average pore diameter of PILMNT-MW10-US20 calculated using the BJH method was found to be 4.0 nm.

The surface area and micropore volume of MNT, PILMNT-24R and PILMNT-MW10-US20 are shown in Table 1. The increase in surface area and decrease in micropore volume of PILMNT-MW10-US20 can be explained by the decrease in crystallite size as calculated from XRD analysis.

2.3. Methods and materials

^{1}H NMR was recorded in CCl_4 or $CDCl_3$ on a 300 MHz Bruker instrument using TMS as the internal standard reference. IR spectra were recorded on a Perkin-Elmer 337 spectrometer. Microwave irradiation carried out in a domestic microwave oven, BPL BMO 700T, India. The ZrO_2-pillared clay was prepared by pillaring of Na^+-montmorillonite clay sample provided by Kunimine Co. Ltd., Japan. Alcohols and acetic anhydride were purchased from Aldrich, USA. $ZrOCl_2 \cdot 8H_2O$ was purchased from S.D. Fine Chemicals, India. For sonochemical intercalation model 3150 DTH (Branson Cleaning Bath, USA) was used. XRD analysis was done using Rigaku D-Max IIIC using Ni-filtered Cu Kα radiation. X-ray fluorescence dispersive spectrophotometer was used to find the zirconium content. BET equation was used to obtain the surface area from the nitrogen adsorption isotherms done on Coulter SA3100 instrument. The average pore diameter of PILMNT-MW10-US20 was calculated using the BJH method. The crystallite sizes were calculated using the Scherrer equation.

2.4. Typical experimental procedure

1,4-Butanediol (0.36 gm, 1 mmol) was added to Zr-PILC (200 mg) and acetic anhydride (0.44 gm, 1.1 mmol) in a beaker (50 ml) covered with a watch glass and irradiated in a microwave oven at power level 9 (640 W) for 10 min. Completion of the reaction was monitored by TLC. The reaction
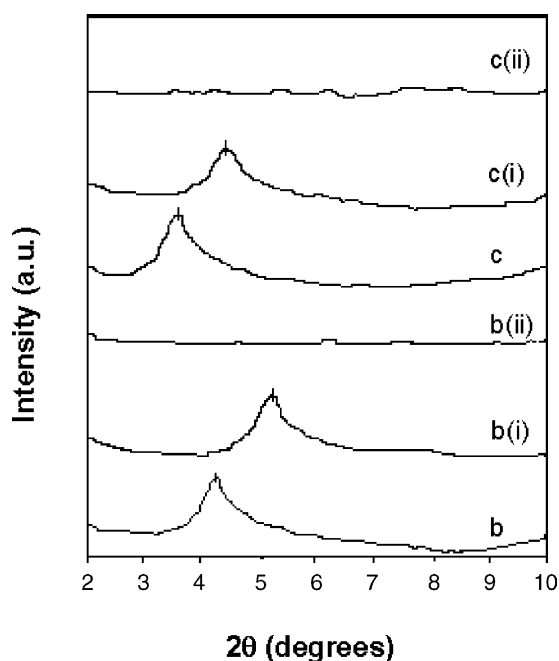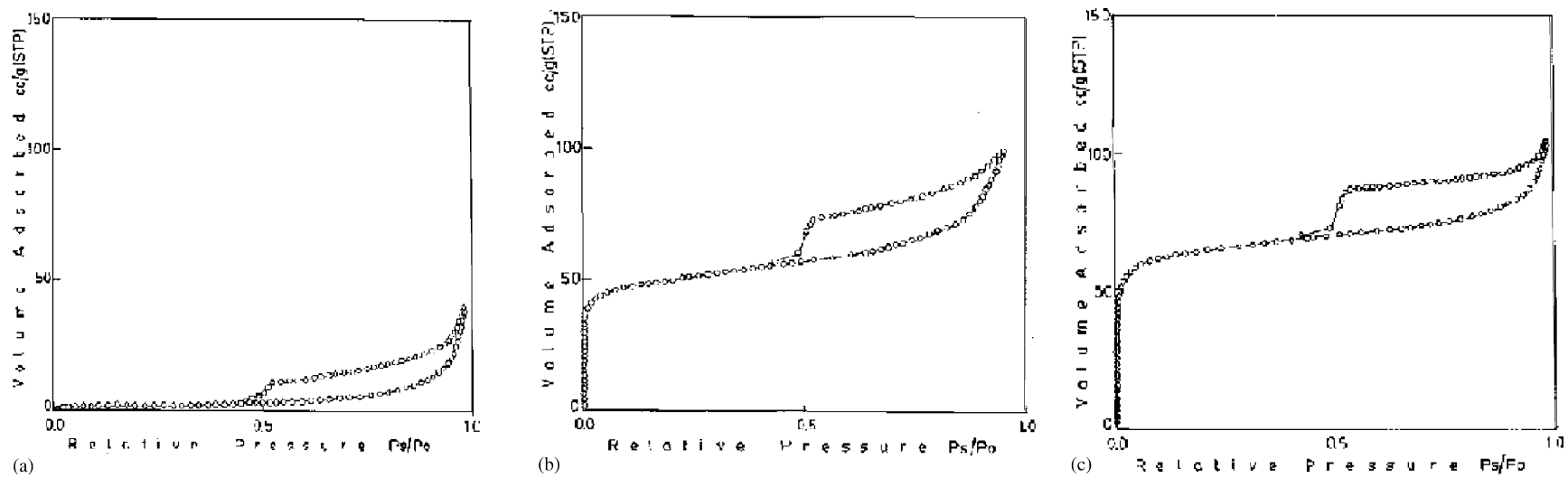

Fig. 2. XRD patterns of (b) PILMNT-24R (120 °C), (b(i)) PILMNT-24R (550 °C), (b(ii)) PILMNT-24R (750 °C), (c) PILMNT-MW10-US20 (120 °C), (c(i)) PILMNT-MW10-US20(550 °C) and (c(ii)) PILMNT-MW10-US20 (750 °C).

Fig. 3. Adsorption–desorption isotherms for nitrogen of (a) MNT (parent clay), (b) PILMNT- 24R and (c) PILMNT-MW10-US20.

Table 1

Results of the MNT, PILMNT-24R and PILMNT-MW10-US20 samples of clay

Sample	d_{001} (Å)		Crystallite size (in nm)	Zr content (mass%)	S_{BET} (m^2/g)	Micropore vol. (cm^3/g)	Weight loss at 550 °C (wt.%)
	Air-dried	550 °C					
MNT	12.9	7.0	17.3	Nil	31	0.053	12.1
Zr-PILMNT (24R)	21.0	19.7	13.8	15.5	155	0.198	22.2
Zr-PILMNT(MW10-US20)	22.1	21.0	8.7	16.4	224.2	0.152	24.1

Note: The natural Na-montmorillonite (Kunipia-F) was used without any further purification for the preparation of Zr-pillared clay. (∗) The microwave heating was done for 10 min of a solution of ZrOCl$_2$ (0.1 M).

Table 2

Mono-acylation of different diols with acetic anhydride over Zr-PILC by microwave irradiation at 640 W (power level 9)

S. no.	Diols	Reaction conditions		Total conversion (%)	Product ratio mono:diacetate (%)	
		Ac$_2$O (eq.)	MWI time (min)			
1	HO(CH$_2$)$_3$OH	1.1	10	70	92	8
2	HO(CH$_2$)$_4$OH	1.1	10	76	95	5
3	HO(CH$_2$)$_5$OH	1.1	15	75	93	7
4	HO(CH$_2$)$_6$OH	1.2	15	73	94	6
5	HO(CH$_2$)$_8$OH	1.5	15	83	95.5	4.5
6	HO(CH$_2$)$_9$OH	1.5	15	77	97	3
7	HO(CH$_2$)$_{10}$OH	2.2	20	75	98.5	1.5

$$ROH + (CH_3CO)_2O \xrightarrow[\text{Microwave Irradiation}]{\text{Zr-PILC}} ROOCCH_3$$

Scheme 1.

mixture was filtered, extracted with ether (2 × 10 ml) and dried over anhydrous Na$_2$SO$_4$. Removal of solvent followed by column chromatography over silica gel using petroleum ether:ether (8:2) gave the desired mono-acylated product (0.35 g, 95%) as shown in Table 2. The samples were analysed by ^{1}H NMR and IR techniques. The catalyst was activated again by microwave irradiation for 20 min at power level 9 (640 W) and recycled for the same reaction, which yielded the desired products in similar ratios without any loss in activity and change in selectivity.

^{1}H NMR (CDCl$_3$): (i) mono-acylated product (major): δ 1.55–1.69 (dq, 4H), 2.1 (s, 3H), 3.56 (t, 2H), 4.1 (t, 2H), D$_2$O exchangeable peak of –OH within the triplet of 2H protons at δ 3.56. (ii) Di-acylated product (minor): δ 1.55–1.69 (dq, 4H), 2.1 (s, 3H), 4.15 (t, 4H), No change in spectra on D$_2$O exchange (Schemes 1 and 2).

3. Results and discussion

This present methodology illustrates a simple process for preparation of ZrO$_2$-pillared clay in 30 min. duration of time
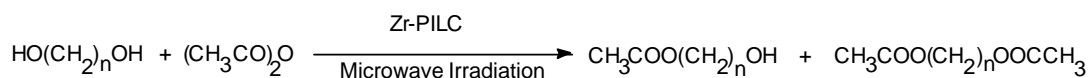
overcoming the problem of long processing time and hence widening the possibilities of its application to various catalytic reactions. It is also the first report of the use of both microwaves heating for preparation of zirconium polyoxycationic species and ultrasound for the intercalation process. The catalyst prepared has improved physico-chemical characteristics in terms of higher surface area and thermal stability. The critical parameters include time of activation by both microwaves and ultrasound, which were optimised to obtain the best results. The catalytic mono-acylation of 1,n-diols in excellent yields under solventless conditions is an economical, environmental friendly methodology and is a significant achievement with the advantages of reduced reaction time as given in Table 2. Moreover, the catalyst can be recycled

Table 3

Acylation of different alcohols with acetic anhydride over Zr-PILC by microwave irradiation at 640 W (power level 9)

S. no.	Reaction conditions			
	Alcohols	Ac$_2$O (eq.)	MWI time (min)	Product yield (%)
1	CH$_3$(CH$_2$)$_3$OH	1.1	5	97
2	CH$_3$(CH$_2$)$_4$OH	1.1	5	98
3	CH$_3$(CH$_2$)$_5$OH	1.1	5	99
4	CH$_3$(CH$_2$)$_2$CHOHCH$_3$	1.2	5	85
5	(CH$_3$)$_3$COH	1.5	5	41
6	C$_6$H$_5$CH$_2$OH	1.2	5	80

$$HO(CH_2)_nOH + (CH_3CO)_2O \xrightarrow[\text{Microwave Irradiation}]{\text{Zr-PILC}} CH_3COO(CH_2)_nOH + CH_3COO(CH_2)_nOOCCH_3$$

Scheme 2.

several times without any loss in activity. The yields, percentage conversion and selectivity depends on the amount of catalyst, acetic anhydride used, time and power of microwave irradiation which were all optimised to standardise the process. Acylation of 1°, 2°, 3° and benzylic alcohols gave the respective acetates and are illustrated in Table 3. K-10 and KSF clay were also used for mono-protection of symmetrical 1,*n*-diols yielding a mixture of products with negligible selectivity.

4. Conclusions

We conclude that we have successfully optimised the preparation of ZrO_2-pillared clay PILMNT-MW10-US20 with enhanced surface area and interlayer spacing with good thermal stability by the rapid and uniform heating effect of microwaves in conjunction with the microstreaming effect of ultrasonic activation to obtain the desired material in 30 min with significant reduction in processing time. The catalytic activity of these clays has been examined for acylation of various primary, secondary, tertiary and benzylic alcohols and mono-acylation of 1,*n*-diols with acetic anhydride under solventless conditions using catalytic amount of ZrO_2-pillared clay with advantages of operational simplicity, recyclibility and selectivity. This methodology can be also used for multistep synthesis of natural products and is an environmentally benign alternative to the existing processes with commercial applications.

Acknowledgements

References

[1] S. Yamanaka, G.W. Brindley, Clay Clay Min. 21 (1978) 26.
[2] R.T. Yang, M.S.A. Baksh, AIChE J. 37 (1991) 679.
[3] R. Burch, Catal. Today 2 (1988) 185.
[4] (a) G.J.J. Bartley, R. Burch, Appl. Catal. 28 (1986) 209;
(b) R.J. Lussier, J.S. Magee, D.E.W. Vanghan, in: S.E. Wanke, S.K. Chakrabarty (Eds.), Proceedings of 7th Canadian Symposium in Catalysis, Chemical Institute of Canada, 1980, 80 pp;
(c) F. Figueras, Catal. Rev. Sci. Eng. 30 (1988) 451.
[5] (a) D.E.W. Vanghan, R.J. Lussier, J.S. Magee, US Patent 4,176,090 (1979);
(b) S. Yamanka, G.W. Brindley, Clay Clay Min. 27 (1979) 119.
[6] M.A. Vicente, M.A. Banases-Munoz, L.M. Gandia, A. Gil, Appl. Catal. A: Gen. 217 (2001) 191.
[7] (a) E.B. Flint, K.S. Suslick, Science 253 (1991) 1397;
(b) T.J. Mason, Advances in Sonochemistry, vol. 1–2, JAI Press, London, 1991/1992;
(c) G. Fetter, G. Heredia, A.M. Maubert, P. Bosch, J. Mat. Chem. 6 (1996) 1857.
[8] S.P. Katdare, V. Ramaswami, A.V. Ramaswami, J. Mat. Chem. 7 (1997) 2197.
[9] C. Vijaya, K. Rengaraj, B. Sivasauleae, Indian J. Chem. 38A (1999) 119.
[10] A.M. De Andies, J. Merino, J.C. Galvan, E. Ruiz-Hitzky, Mat. Res. Bull. 34 (1999) 541.
[11] (a) T.W. Greene, P.G.M. Wuts, Protective Groups in Organic Synthesis, second ed., Wiley, New York, 1991;
(b) S.G. Wilkinson, in: Comprehensive Organic Chemistry, vol. 1, Pergamon Press, New York, 1979, p. 681.
[12] P.G. McDougal, J.G. Rico, Y.-I. Oh, B.D. Condon, J. Org. Chem. 51 (1986) 3388.
[13] (a) H. Weber, H.G. Khorana, J. Mol. Biol. 72 (1972) 219;
(b) R.I. Zhdanov, S.M. Zhenodarova, Synthesis (1975) 222;
(c) G. Stork, T. Takahashi, I. Kawamoto, T. Suzuki, J. Am. Chem. Soc. 100 (1978) 8272.
[14] J.H. Babler, M.J. Coghlan, Tetrahedron Lett. (1979) 1971.
[15] G. Hofle, W. Steglick, H. Vorbruggen, Angew. Chem. Int. Ed. Engl. 17 (1978) 569.
[16] (a) H. Ogawa, T. Chihara, K. Taya, J. Am. Chem. Soc. 107 (1985) 1365;
(b) H. Ogawa, Y. Ichimura, T. Chihara, S. Teratani, K. Taya, Bull. Chem. Soc. Jpn. 59 (1986) 2481;
(c) H. Ogawa, T. Chihara, S. Teratani, K. Taya, J. Chem. Soc., Chem. Commun. (1986) 1337.
[17] S. Fujisaki, Y. Ishii, Y. Yano, A. Nishida, J. Org. Chem. 59 (1994) 1191.
[18] J.D.L. Zerda, G. Barak, Y. Sasson, Tetrahedron Lett. 29 (1989) 1533.
[19] C.C. Leznoff, Acc. Chem. Res. 11 (1989) 327.
[20] M. Balogh, P. Laszlo, Organic Chemistry Using Clays, Springer-Verlag, New York, 1993.
[21] A. Loupy, A. Petit, J. Hamelin, F. Texier-Boullet, P. Jacqualt, D. Mathe, Synthesis (1998) 1213.
[22] (a) A. Loupy, Top. Curr. Chem. 206 (1999) 155;
(b) R.S. Varma, Clean Products and Processes, Springer-Verlag, New York, 1999, p. 132.
[23] (a) R. Latouche, F. Texier-Boullet, J. Hamelin, Tetrahedron Lett. 32 (1991) 1179;
(b) G. Bram, A. Loupy, M. Majdoub, E. Ruiz-Hitzky, Tetrahedron 46 (1990) 5167;
(c) B. Rechsteiner, F. Texier-Boullet, J. Hamelin, Tetrahedron Lett. 34 (1993) 5071;
(d) B. Touax, B. Klein, F. Boullet, J. Hamelin, J. Chem. Res. (S) (1994) 116;
(e) G.L. Kad, J. Kaur, P. Bansal, J. Singh, J. Chem. Res. (S) (1996) 188.
[24] K. Smith, Solid Support and Catalysis in Organic Synthesis, Ellis Harwood, Chichester, 1992.
[25] (a) V. Singh, V. Sapehiyia, G.L. Kad, Synthesis (2003) 198;
(b) V. Singh, A. Khurana, K. Kaur, G.L. Kad, Resonance (1998) 56;
(c) V. Singh, S. Choudhary, G.L. Kad, J. Singh, Ultrason. Sonochem. (2001) 123.
[26] (a) V. Singh, A. Khurana, V. Sapehiyia, I. Kaur, G.L. Kad, J. Chem. Soc., Perkin Trans. 1 (2002) 1766;
(b) G.L. Kad, Vasundhara Singh, A. Khurana, J. Singh, J. Chem. Res. (S) (1999) 164;
(c) G.L. Kad, V. Singh, K. Kaur, J. Singh, Tetrahedron Lett. 36 (1997) 1079.
[27] K.S.W. Singh, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Piesotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. 57 (1985) 603.