Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Molecular Catalysis A: Chemical 212 (2004) 237–243
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Microencapsulated bismuth(III) triflate catalyst for organic transformations

B.M. Choudary*, Ch. Sridhar, M. Sateesh, B. Sreedhar

Inorganic Chemistry and Physical Chemistry Division, Indian Institute of Chemical Technology, Tarnaka, Hyderabad 500 007, India

Received 14 August 2003; accepted 27 October 2003

Abstract

A recoverable and reusable polymer encapsulated bismuth(III) triflate catalyst, designed and developed for the first time for effective allylation of aldehydes, Michael type addition of aliphatic amines to α,β-ethylenic compounds, acylation of alcohols, Baeyer–Villiger oxidation and aldol condensation, exhibited truly heterogeneous nature throughout the reaction.

Keywords: Bismuth(III) triflate; Microencapsulation; Heterogeneous catalyst; Organic transformations; XPS

1. Introduction

The heterogenisation of inorganic reagents and catalysts that are useful in organic reactions is an important goal in clean technology [1]. The utility of heterogenised polymer catalysts is now well recognised, because of their ease of work up and separation of product from the catalyst. Kobayashi et al. reported a novel microencapsulation technique for the immobilisation of OsO_4, $Pd(PPh_3)_4$, $Sc(OTf)_3$ and arene–ruthenium complexes in the pores of polystyrene to obtain easy recoverable and reusable catalysts for very important organic transformations [2a-i]. Recently, $VO(acac)_2$ encapsulated in polystyrene is used for epoxidation of allyl alcohols [2g]. The microencapsulated metal complex is physically enveloped by a thin film of a polymer usually polystyrene and stabilised by the interaction between π-electrons of the benzene ring of the polystyrene and vacant orbitals of metal. However, the heterogeneity and mechanism of the reaction mediated by the microencapsulated catalysts have not yet been investigated. Recently, bismuth(III) triflate [$Bi(OTf)_3$] has received great interest, because it is an easily obtained inexpensive material from commercially available bismuth(III) oxide and triflic acid [3], and has ubiquitous applications in many organic transformations [4,5]. We describe herein the design and development of the recoverable and reusable polymer encapsulated $Bi(OTf)_3$ catalyst for the first time for effective allyaltion of aldehydes, Michael type addition of aliphatic amines to α,β-ethylenic compounds, acylation of alcohols, Baeyer–Villiger oxidation and aldol condensation. The catalyst exhibits truly heterogeneous nature through out the reaction.

2. Experimental

2.1. General

The chemical shifts (δ) are reported in ppm, using TMS as an internal standard and $CDCl_3$ as solvent. The samples were mounted on copper grid by ultrasonification. X-ray photoemission spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg K anode. The pressure in the spectrometer was about 10^{-9} Torr. For energy calibration we have used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 285.0 eV. Spectra were deconvoluted using Sun Solaris based Vision 2 curve resolver. The location and the full-width at half maximum (FWHM) for a species was first determined using the spectrum of a pure sample. The location and FWHM of products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible

* Corresponding author. Tel.: +91-40-2719-1510; fax: +91-40-2716-0921.
E-mail addresses: choudary@iict.res.in, bmchoudary@yahoo.com (B.M. Choudary).

1381-1169/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2003.10.037

to within ± 0.1 eV. TGA–MS thermograms were recorded on Mettler–Toledo TGA/SDTA 821[e] instrument coupled to Balzers Thermostar GSD 300 T in the temperature range 25–1000 °C with a heating rate of 10 °C/min in nitrogen atmosphere. Atomic absorption spectroscopy (AAS) analysis was on Perkin–Elmer A Analyst 300. scanning electron microscopy–energy dispersive (SEM–EDX) X-ray analysis was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument. Thin layer chromatography was performed on Merck precoated silica gel 60-F_{254} plates.

Polystyrene (M_w: ca. 280,000), allyltributytin and trifluoromethanesulfonic acid was purchased from Aldrich. Bismuth(III) triflate was prepared according to the literature procedure [3]. All acrylates and aldehydes purchased from Fluka. All other solvents and chemicals were obtained from commercial sources and used as such without further purification.

2.2. Preparation of microencapsulated bismuth(III) triflate

Microencapsulated bismuth(III) triflate [MCBi(OTf)$_3$] was prepared by using the standard microencapsulated procedure [6]: Polystyrene (1.0 g, M_w: 280,000) was dissolved in cyclohexane (20 ml) at 40 °C, and to this solution was added powdered Bi(OTf)$_3$ (0.2 g) as a solid core. The mixture was stirred for 1 h at this temperature and then slowly cooled to 0 °C. Co-acervates were found to envelop the solid core dispersed in the medium, and hexane (30 ml) was added to harden the capsule walls. The mixture was stirred at room temperature for 1 h and the capsules were washed with acetonitrile several times and dried at 50 °C for 3 h. The unreacted Bi(OTf)$_3$ (20 mg) was recovered and found that 180 mg of Bi(OTf)$_3$ was encapsulated in polystyrene.

2.3. Characterisation

Scanning electron microscope (SEM) studies suggest that the capsules of MCBi(OTf)$_3$ adhered to each other, probably due to small size of the core. The FTIR spectra of the MCBi(OTf)$_3$ shows all the peaks of bismuth(III) triflate and polystyrene, indicating the encapsulation of Bi(OTf)$_3$ [5d,7].

IR (KBr) MCBi(OTf)$_3$: 3056, 3018 (νCH), 1946, 1868, 1794 (δCH), 1601, 1493 (benzene rings), 1254 ($\nu_{as}SO_2$), 1045 ($\nu_S SO_2$), 748 (νC–S), 640 (νS–O) cm^{-1}.

Bi(OTf)$_3$: 1290 ($\nu_{as}SO_2$), 1032 ($\nu_S SO_2$), 766 (νC–S), 656 (νS–O) cm^{-1}.

The TGA–DTA thermograms of Bi(OTf)$_3$ and MCBi(OTf)$_3$ show two endotherms at 100, 420 and 120, 450 °C, respectively, under identical conditions and the display of the small shift in both the endotherms [8] is attributed to the weak interactions between Bi(OTf)$_3$ and support.

XPS of the MCBi(OTf)$_3$ catalyst (Fig. 1, Survey scan) exhibits Bi $2p_{3/2,1/2}$ lines at 160, 165.3 and 160, 165.3 eV which is in close agreement with that of Bi(OTf)$_3$ at 160.9, 166.3 and 160.5, 165.8 respectively. The XPS spectra of C 1 s of the MCBi(OTf)$_3$ catalyst in Fig. 2 exhibits three lines on deconvolution at 284.1, 285.2 and 292.6 eV, corresponding to the carbon impurity due to the pump oil, polystyrene, and CF_3, respectively The XPS of the Bi(OTf)$_3$, MCBi(OTf)$_3$ catalyst show almost identical pattern for S and F.

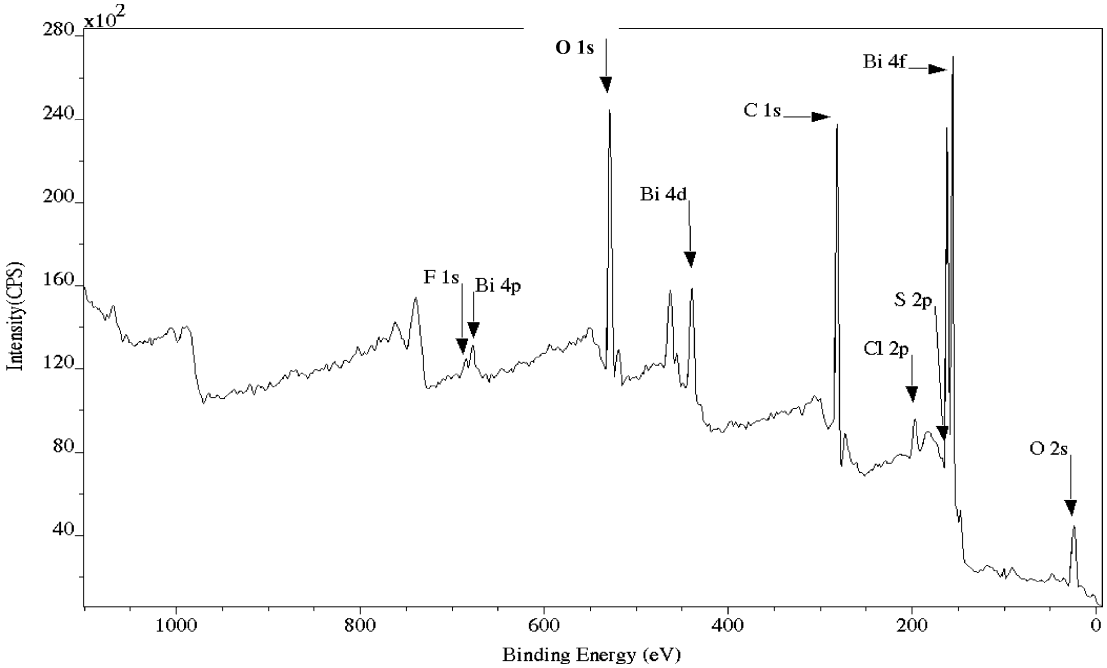


Fig. 1. XPS survey scan of MCBi(OTf)$_3$.

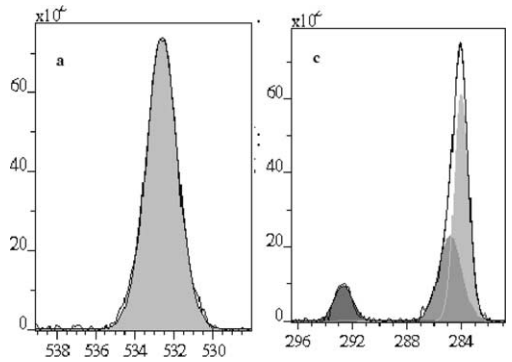


Fig. 2. XPS deconvoluted spectra of oxygen and carbon in $MCBi(OTf)_3$ (a) O 1s peak of $MCBi(OTf)_3$ and (b) C 1s peak of $MCBi(OTf)_3$.

2.4. Typical experimental procedures

2.4.1. General procedure for allylation of aldehydes

To $MCBi(OTf)_3$ (100 mg) was added a mixture of *p*-chlorobenzaldehyde (1 mmol), benzoic acid (1 mmol) and allyltributylstannane (1.2 mmol) in acetonitrile (5 ml) at room temperature, and the mixture was stirred for a specified period. The progress of the reaction was monitored by TLC and on completion of the reaction, the reaction mixture is filtered and the filtrate was concentrated under vacuum and subjected to column chromatography (10% ethyl acetate/hexane) to get the pure product (164 mg, 90%). ^{1}H NMR (200 MHz, $CDCl_3$) δ2.52 (m, 2H, CH_2), 4.75 (t, 1H,CH), 5.14–5.20 (m, 2H, 2 vinyl's), 5.82 (m, 1H, vinyl), 7.2–7.3 (m, 4H, aromatic).

2.4.2. General procedure for addition of aliphatic amines to α,β-ethylenic compounds

To $MCBi(OTf)_3$ (50 mg) was added a mixture of piperazine (1 mmol), methyl acrylate (2 mmol) in acetonitrile (5 ml) at room temperature, and the mixture was stirred for a specified period. The progress of the reaction was monitored by TLC and on completion of the reaction, the reaction mixture is filtered and the filtrate was concentrated under vacuum the filtrate was concentrated under reduced pressure to get the pure product (245 mg, 95%). ^{1}H NMR (200 MHz, $CDCl_3$) δ2.45–2.55 (m, 12H), 2.69 (m, 4H).

2.4.3. General procedure for acetylation of alcohols

To $MCBi(OTf)_3$ (50 mg) was added a mixture of 2-phenylethanol (1 mmol), acetic anhydride (2 mmol) in acetonitrile (5 ml) at room temperature, and the mixture was stirred for a specified period. The progress of the reaction was monitored by TLC and on completion of the reaction, the reaction mixture is filtered and the filtrate was washed with saturated sodium bicarbonate and brine, dried on anhydrous magnesium sulphate and concentrated under vacuum to obtain the pure product (155.8 mg, 95%). ^{1}H NMR (200 MHz, $CDCl_3$) δ0.5–0.6 (d, 3H), 2.1 (s, 3H), 5.8–5.95 (q, 1H), 7.25–7.4 (m, 5H).

2.4.4. General procedure for Baeyer–Villiger oxidation

To $MCBi(OTf)_3$ (100 mg) was added a mixture of cyclohexanone (1 mmol), *m*-CPBA (2 mmol) in acetonitrile (5 ml) at room temperature, and the mixture was stirred for a specified period. The progress of the reaction was monitored by TLC and on completion of the reaction, the reaction mixture is filtered and the filtrate was concentrated under vacuum and subjected to column chromatography (10% ethyl acetate/hexane) to get the pure product (96 mg, 90%). ^{1}H NMR (200 MHz, $CDCl_3$) δ4.0 (t, 2H), 2.4 (t, 2H), 1.8 (m, 4H).

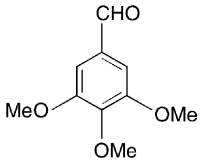
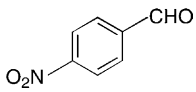
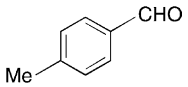
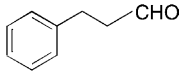
2.4.5. General procedure for aldol condensation

To $MCBi(OTf)_3$ (100 mg) was added 4-nitro benzaldehyde (1 mmol) in acetone (5 ml) at room temperature, and the mixture was stirred and the mixture was stirred for a specified period. The progress of the reaction was monitored by TLC and on completion of the reaction, the reaction mixture is filtered and the filtrate was concentrated under vacuum to get the pure product (175 mg, 90%). ^{1}H NMR (200 MHz, $CDCl_3$): δ2.2 (s, 3H), 2.8 (d, 2H), 3.6–3.8 (OH, 1H), 5.2 (t, 1H), 7.6 (d, 2H), 8.2 (d, 2H).

3. Results and discussion

The $MCBi(OTf)_3$ thus obtained is evaluated for allylation of aldehydes, Michael type addition of aliphatic amines to α,β-ethylenic compounds, acylation of alcohols, Baeyer–Villiger oxidation and aldol condensation. A perfect correlation between the conversions in homogeneous

Table 1
$MCBi(OTf)_3$ catalyzed allylation of aldehydes[a]

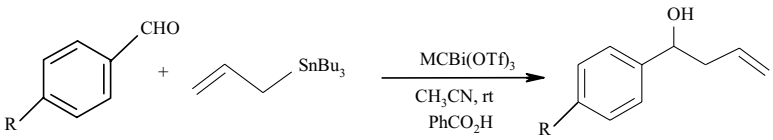
Entry	Aldehyde	Time (min)	Yield (%)[b]
1		20	95
		5 (110)	95[c] (88)
2		20	90
		5 (90)	95[c] (93)
3		30	90
4		40	80

The values in parentheses refer to the $La(OTf)_3$ catalysed reaction.

[a] Reaction conditions: 1 mmol of aldehyde, 1.5 mmol of allyltributyistannane, 100 mg of $MCBi(OTf)_3$, 1 mmol of benzoic acid, 5 ml acetonitrile.

[b] Yields based on isolated yields.

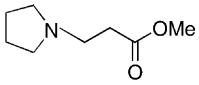
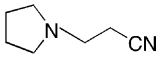
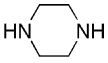
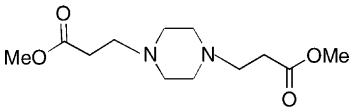
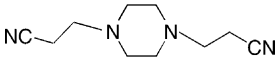
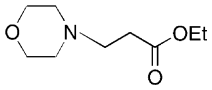
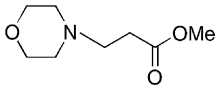
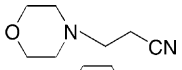
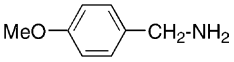
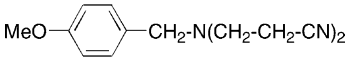
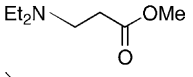
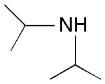
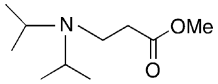
[c] With $Bi(OTf)_3$.

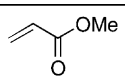
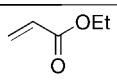


Scheme 1. The allylation of aldehydes with allyltributylstannane by $MCBi(OTf)_3$

and heterogenised conditions can be observed, therefore, the activity of the catalyst does not decay upon encapsulation. The Lewis acid (LA) catalysed allylation of aldehydes (Scheme 1) has become an important C–C bond forming reactions in organic synthesis [9], because the reaction adds a new functionality into the substrate that can be extended to further organic transformations. Benzoic acid acts as a rate accelerating agent and in the absence of benzoic acid the reaction is very slow. Addition of one equivalent of benzoic acid would rapidly destroy the alkoxide, thus immediately restoring the activity of the Lewis acid [9d]. $MCBi(OTf)_3$ shows higher activity than $MCSc(OTf)_3$ and almost similar activity as homogeneous $Bi(OTf)_3$ [10]. The atomic absorption spectroscopy of the filtrate of the reaction mixture of the first cycle shows the presence of a very small amount (<1 ppm) of the bismuth, indicating that there was almost no leaching of $Bi(OTf)_3$ from the $MCBi(OTf)_3$. The catalyst was separated by simple filtration and reused for four cycles without significant loss of activity. The result of such leaching of active constituent is in consonance with

Table 2
$MCBi(OTf)_3$ catalysed Micheal type addition of aliphatic amines[a]

Entry	Reagent	Ethylenic compound	Product	Time (min)	Yield (%)[b]
1		A		10	96
		B		15	92
				15	90[c]
2		A		30	95
		B		25	95 (76)
				120	40[d]
		C		45	90
3		A		30	95
		B		30	94
4		B		180	54
5	Et_2NH	A		40	95
6		A		55	95

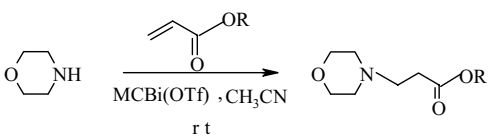
Ethylenic compounds:  A  B  C

[a] Reaction conditions: 1 mmol amine, 2 mmol ethylenic compound, 50 mg $MCBi(OTf)_3$, 5 ml acetonitrile, RT.
[b] Yields based on isolated yields.
[c] Yield after third cycle.
[d] Without catalyst.

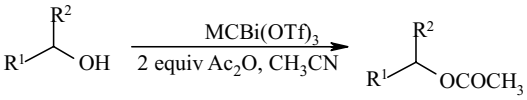
the earlier reports on microencapsulated catalysts [2]. To understand the scope and reactivity, we carried out the allylation of a variety of aldehydes, which affords very good yields (Table 1).

One of the simplest potential routes for the synthesis of β-amino derivatives such as β-amino esters is via the Lewis acid-mediated addition (chemical activation) of amines to α,β-ethylenic compounds [11]. However, only simple primary amines can react with simple unsubstituted acrylic compounds without special activation such as high temperature, high pressure, the use of appropriate catalysts etc. [12]. Matsubara et al. reported Michael type addition reaction using $Yb(OTf)_3$ which also worked well equally with aliphatic as well as aromatic amines. A new catalytic system utilising clay has been recently reported for the chemoselective addition of aliphatic amines to α,β-ethylenic compounds [13], here we wish to report the addition of aliphatic amines to α,β-ethylenic compounds using $MCBi(OTf)_3$ as a catalyst (Table 2). This catalyst shows higher activities when compared with the reported clay catalyst (Table 2, entry 2). The atomic absorption spectroscopy of the filtrate of the reaction mixture of the first cycle shows the presence of a very small amount (3.47 ppm) of the bismuth, indicating that there was almost no leaching of $Bi(OTf)_3$ from the $MCBi(OTf)_3$. The catalyst was recovered by simple filtration and reused for three cycles without significant loss in activity (Scheme 2).

The acylation of alcohols is an important transformation in organic synthesis [14]. Conversion of an alcohol to the corresponding acetate is typically carried out by using acetic anhydride or acetyl chloride in the presence of pyridine or triethylamine base as a catalyst in addition of these amine bases many Lewis acids are known to catalyse this reaction [15]. Most of these processes suffer by two reasons, one is metals used are toxic and another is triflates are very expensive. Recently, the use of bismuth triflate as a catalyst for the acylation of alcohols has been reported [16]. There is need to develop heterogeneous catalyst for the acetylation of alcohols to overcome the above mentioned problems. $MCBi(OTf)_3$ catalyst promotes the acetylation of primary and secondary alcohols with acetic anhydride in acetonitrile solvent at room temperature. Interestingly, Primary and secondary alcohols undergo selective acetylation with this heterogeneous catalyst in the presence of aromatic alcohols. This selectivity was not observed in the case of homogeneous $Bi(OTf)_3$ catalyst. The atomic absorption spectroscopy of the filtrate of the reaction mixture of the first cycle shows the presence of a very small amount (5.7 ppm) of the bismuth, indicating that there was almost no leaching of $Bi(OTf)_3$ from the $MCBi(OTf)_3$. $MCBi(OTf)_3$ recovered

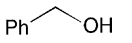
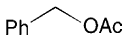
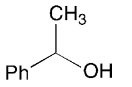
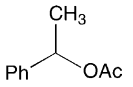
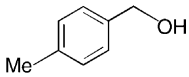
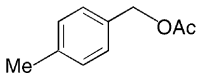
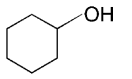
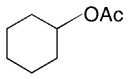
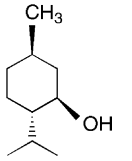
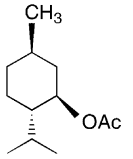
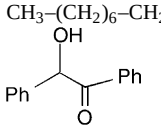
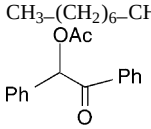


Scheme 2. The Michael type addition of aliphatic amines by $MCBi(OTf)_3$.



Scheme 3. Acylation of alcohols with acetic anhydride by $MCBi(OTf)_3$.

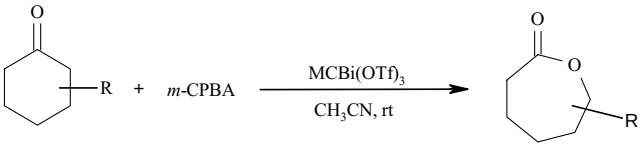
Table 3
$MCBi(OTf)_3$ catalysed acylation of alcohols[a]

Entry	Alcohol	Product	Time (min)	Yield (%)[b]
1			30	90
			30	85[c]
2			20	95
3			20	90
4			50	80
5			30	80
6	CH_3–$(CH_2)_6$–CH_2OH	CH_3–$(CH_2)_6$–CH_2OAc	60	75
7			60	85

[a] Reaction conditions: 1 mmol alcohol, 2 mmol acetic anhydride, 50 mg $MCBi(OTf)_3$, 5 ml acetonitrile, RT.
[b] Yields based on isolated yields.
[c] Yield after third cycle.

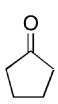
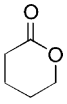
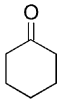
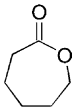
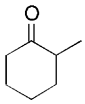
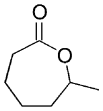
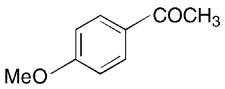
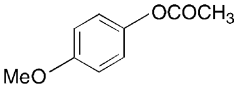
by simple filtration and reused for three cycles without significant loss in activity (Scheme 3, and Table 3).

Baeyer–Villiger oxidation has been widely applied in organic synthesis for the oxidation of ketones to esters or lactones using peracids or hydrogen peroxide [17]. Among the peracids, *m*-CPBA is widely used but it requires prolonged reaction time. In conjunction with *m*-CPBA, $MCBi(OTf)_3$ displays comparable activity as shown by $Sc(OTf)_3$ for Baeyer–Villiger oxidation (Scheme 4) of the ketone in acetonitrile leading to the corresponding lactone. $MCBi(OTf)_3$ was recovered by simple filtration and reused for three cycles without significant loss in activity to demonstrate that the catalyst is robust, despite adverse oxidative environment. The atomic absorption spectroscopy of the filtrate of the reaction mixture of the first cycle shows the presence of



Scheme 4. Baeyer–Villiger oxidation of ketones with *m*-CPBA by $MCBi(OTf)_3$.

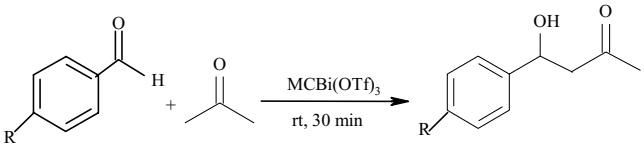
Table 4
$MCBi(OTf)_3$ catalysed Baeyer–Villiger oxidations[a]

Entry	Substrate	Product	Time (min)	Yield (%)[b]
1			40	90
2			60	85
3			40	90
4			120	60

[a] Reaction conditions: 1 mmol ketone, 2 mmol *m*-CPBA, 100 mg $MCBi(OTf)_3$, 5 ml acetonitrile, RT.
[b] Yields based on isolated yields.

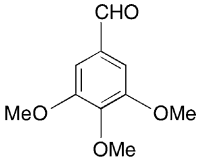
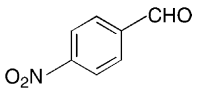
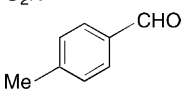
a very small amount (2.2 ppm) of the bismuth, indicating that there was almost no leaching of $Bi(OTf)_3$ from the $MCBi(OTf)_3$. Encouraged by this result, we have carried out the Baeyer–Villiger oxidation of variety of ketones and the results are summarised in Table 4.

The aldol condensation is of prime importance for fine chemical synthesis and is generally catalysed by acids or bases. $MCBi(OTf)_3$ was successfully used in aldol condensation of 4-nitrobenzaldehyde with acetone to afford the corresponding aldol product with 90% yield (Scheme 5) and



Scheme 5. Aldol condensation of aldehydes with acetone by $MCBi(OTf)_3$.

Table 5
$MCBi(OTf)_3$ catalysed aldol condensation[a]

Entry	Aldehyde	Time (min)	Yield (%)[b]
1		40	90
2		30	90
3		50	85

[a] Reaction conditions: 1 mmol aldehyde, 5 ml acetone,100 mg $MCBi(OTf)_3$, RT.
[b] Yields based on isolated yields.

the catalyst was used for three cycles without significant loss in activity. Encouraged by this result, we have carried out the aldol condensation of variety of aldehydes in order to understand the scope and reactivity. The atomic absorption spectroscopy of the filtrate of the reaction mixture of the first cycle shows the presence of a very small amount (4.4 ppm) of the bismuth, indicating that there was almost no leaching of $Bi(OTf)_3$ from the $MCBi(OTf)_3$. The results are summarised in Table 5.

4. Conclusions

In conclusion, we have prepared recoverable and reusable microencapsulated bismuth(III) triflate and found effective in many reactions. For the first time we are able to provide the reaction sequence on the heterogenised catalyst demonstrating the true heterogeneity of the $MCBi(OTf)_3$ and unfolding the mechanism for the allylation of aldehydes.

Acknowledgements

Ch.S. and M.S. thank the Council of Scientific and Industrial Research, India, for their fellowships.

References

[1] J.H. Clark, Catalysis of Organic Reactions using Supported Inorganic Reagents, VCH, New York, 1994.
[2] (a) S. Nagayama, M. Endo, S. Kobayashi, J. Org. Chem. 63 (1998) 6094;
(b) S. Kobayashi, S. Nagayama, J. Am. Chem. Soc. 120 (1998) 2985;
(c) S. Kobayashi, M. Endo, S. Nagayama, J. Am. Chem. Soc. 121 (1999) 11229;
(d) R. Akiyama, S. Kobayashi, Angew. Chem. Int. Ed. 40 (2001) 3469;
(e) S. Kobayashi, T. Ishida, R. Akiyama, Org. Lett. 3 (2001) 2649;
(f) R. Akiyama, S. Kobayashi, Angew. Chem. Int. Ed. 41 (2002) 2602;
(g) A. Lattanzi, N.E. Leadbeater, Org. Lett. 4 (2002) 1519;
(h) R. Akiyama, S. Kobayashi, J. Am. Chem. Soc. 125 (2003) 3412 ;
(i) S. Kobayashi, R. Akiyama, Chem. Commun. 4 (2003) 449.
[3] S. Repichet, A. Zwick, L. Vendier, C. Le Roux, J. Dubac, Tetrahedron Lett. 43 (2002) 993.
[4] (a) H. Suzuki, T. Ikegami, Y. Matano, Synthesis 3 (1997) 249;
(b) J.A. Marshall, Chemtracts 10 (1997) 1064;
(c) S. Vidal, Synlett 4 (2001) 1194;
(d) J.R. Desmurs, M. Labrouillere, C. Le Roux, H. Gaspard, A. Laporterie, J. Dubac, Tetrahedron Lett. 38 (1997) 8871;
(e) S. Repichet, C. Le Roux, J. Dubac, Eur. J. Org. Chem. 63 (1998) 2743.
[5] (a) S. Repichet, C. Le Roux, P. Hernandez, J. Dubac, J.R. Desmurs, J. Org. Chem. 64 (1999) 6479;
(b) S. Repichet, C. Le Roux, J. Dubac, Tetrahedron Lett. 40 (1999) 9233;
(c) H. Laurent-Robert, C. Le Roux, J. Dubac, Synlett 10 (1998) 1138;
(d) B. Garrigues, F. Gonzaga, H. Robert, J. Dubac, J. Org. Chem. 62 (1997) 4880;
(e) H. Robert, B. Garrigues, J. Dubac, Tetrahedron Lett. 39 (1998) 1161;

(f) A. Orita, C. Tanahashi, A. Kakuda, J. Otera, Angew. Chem. Int. Ed. 39 (2000) 2877;
(g) S. Gmouh, H. Yang, M. Vaultier, Org. Lett. 5 (2003) 2219.
[6] This is a standard procedure for preparation of microcapsules. M. Donbrow, Microcapsules and Nanoparticles in Medicine and Pharmacy; CRC Press, Boca Raton, 1992.
[7] M. Labrouillere, C. Le Roux, H. Gaspard, A. Laporterie, J. Dubac, Tetrahedron Lett. 40 (1999) 285.
[8] S. Singh, Amita, R.D. Verma, Indian J. Chem. 22A (1983) 814.
[9] (a) M. Pereyre, J.-P. Quintard, A. Rahm, Tin in Organic Synthesis, Butterworths, London, 1987, p. 216.;
(b) Y. Nishigaichi, A. Takuwa, Y. Naruta, K. Maruyama, Tetrahedron 49 (1993) 7395;
(c) Y. Yamamoto, N. Asao, Chem. Rev. 93 (1993) 2207;
(d) H.C. Aspinall, N. Greeves, E.G. Mclver, Tetrahedron Lett. 39 (1998) 9283.
[10] B.M. Choudary, S. Chidara, C.H.V. Raja Sekhar, Synlett 10 (2002) 1694.
[11] T. Ben Ayed, H. Amiri, M. EI Gaied, J. Villieras, Tetrahedron 35 (1995) 9633.
[12] (a) M. Furukawa, T. Okawara, Y. Terawaki, Chem. Pharm. Bull. 25 (1977) 1319;
(b) J. D'Angelo, J. Maddaluno, J. Am. Chem. Soc. 108 (1986) 8112;
(c) S. Matsubara, M. Yoshioka, K. Utimoto, Chem. Lett. 5 (1994) 827;
(d) G. Jenner, Tetrahedron Lett. 36 (1995) 233.
[13] N.S. Shaikh, V.H. Deshpande, A.V. Bedekar, Tetrahedron 57 (2001) 9045.
[14] (a) T.W. Greene, P.G.M. Wuts, Protective Groups in Organic Synthesis, third ed., Wiley, New York, 1999.;
(b) J.R. Hanson, Protecting Groups in Organic Synthesis, first ed., Blackwell Science, Inc, Malden, MA, 1999.;
(c) P.J. Kocienski, Protecting Groups, first ed. Georg Thieme Verlag, Stuttgart, 1994.
[15] (a) R. Kumareswarnan, A. Gupta, Y.D. Vankar, Synth. Commun. 27 (1997) 277;
(b) E. Vedejs, O. Daugulis, J. Org. Chem. 61 (1996) 5702;
(c) K. Ishihara, M. Kubota, H. Yamamoto, Synlett 3 (1996) 265;
(d) M. Miyashita, I. Shiina, S. Miyoshi, T. Mukaiyama, Bull. Chem. Soc. Jpn. 66 (1993) 1516;
(e) J. Iqbal, R.R. Srivastava, J. Org. Chem. 57 (1992) 2001.
[16] M.D. Carrigan, D.A. Freiberg, R.C. Smith, H.M. Zerth, R.S. Mohan, Synthesis 14 (2001) 2091.
[17] G.R. Krow, Tetrahedron 37 (1981) 2697.