Pergamon

Tetrahedron Letters 43 (2002) 6305–6307

TETRAHEDRON
LETTERS

Efficient bismuth catalysts for transcarbamoylation

B. Jousseaume,[a,*] C. Laporte,[a] T. Toupance[a] and J.-M. Bernard[b]

[a]*Laboratoire de Chimie Organique et Organométallique, UMR 5802 CNRS, Université Bordeaux 1, 351, Cours de la Libération, F-33405 Talence Cedex, France*
[b]*Centre de Recherche des Carrières, Rhodia, 85 avenue des Frères Perret, BP 62, F-69192 Saint-Fons, France*

Accepted 10 July 2002

Abstract—Among some bismuth catalysts, bismuth trifluoromethanesulfonate showed excellent catalytical properties in the transcarbamoylation reaction between a *N*-alkyl *O*-alkyl carbamate and a primary alcohol. It was found more active than classical organotin catalysts. Moreover it was also more selective as no alkyl isocyanate was detected during the transcarbamoylation.

The transcarbamoylation reaction has important industrial applications in the field of polyurethane chemistry, especially for coatings.[1] Polyurethanes are usually obtained by mixing two components, polyisocyanates and polyols, which requires their precise metering with expensive equipment and necessitates handling of toxic isocyanates. Another technique involving only one package system appeared recently.[2] It comprises blocked polyisocyanates and polyols which do not react at room temperature, thus providing long pot lives. Upon heating, under the influence of a catalyst, the blocked isocyanate reacts with the polyol to give the polyurethane, with evolution of the blocking agent. One of the most popular blocking agents is methylethylketoxime, which can be used at low temperature, associated with catalysts as cobalt, tin or zinc derivatives for example. However, other blocking agents such as aliphatic alcohols would be advantageous to reduce toxic volatile organic compound (VOC) emissions and costs. To our knowledge aliphatic alcohols have not been used up to now in industry, the stability of *O*-alkyl carbamates necessitating reaction temperatures higher than for other blocking agents as methyl ethyl ketoxime. That is the reason why more active catalysts are searched in order to make possible the use of less toxic but less reactive blocking agents.

In this paper the description of the catalytic properties of bismuth compounds in the transcarbamoylation reaction, compared to other catalysts as organotins and rare-earth compounds is reported.

Bismuth compounds are Lewis acids showing many interesting applications in organic synthesis as catalysts.[3,4] Very recently Dubac used bismuth trifluoromethanesulfonate with great success in the Friedel–Crafts acylations of toluene, benzene and even deactivated chlorobenzene,[5] and in Diels–Alder[6] and aza-Diels–Alder[7] reactions. It was also found very efficient as a catalyst by Otera in the acylation of alcohols with anhydrides.[8]

Bismuth derivatives have already been used in the field of polyurethane synthesis. Triphenylbismuth is known to catalyse the addition of alcohols to isocyanates[9] and several inorganic bismuth compounds or salts such as bismuth oxide, hydroxide or citrate have also been used as catalysts or cocatalysts in transcarbamoylation reactions.[10]

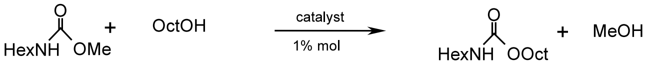
The activity of known organotin catalysts[11] and several bismuth derivatives such as triphenylbismuth, bismuth trichloride or trifluoromethanesulfonate were compared in the transcarbamoylation between *N*-hexyl *O*-methyl carbamate and *n*-octanol in stoichiometric amounts at 122°C. Aliquots of the reaction mixture were removed every 15 min and analysed by GC by comparison with authentic samples. The yield in *N*-hexyl *O*-octyl carbamate was determined using hexadecane as an internal standard (Scheme 1).

For each catalyst investigated, the experimental kinetic curve was fitted by postulating an overall second order of the reaction. Further studies about the orders of the individual reactants revealed that the reaction was first order both in the starting carbamate and alcohol. The

---

* Corresponding author. Fax: +33 556 84 69 94; e-mail: b.jousseaume@lcoo.u-bordeaux.fr

0040-4039/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(02)01391-6



Scheme 1. Transcarbamoylation reaction.

Table 1. Catalysed transcarbamoylation of a *N*-alkyl *O*-alkyl carbamate

Entry	Catalyst	Rate constant[a]	Yield
1	$BiPh_3$	0	0[b]
2	$BiCl_3$	3.8×10^{-5}	2[b]
3	$Bi(O_3SCF_3)_3$	4.5×10^{-3}	70[b]
4	$Bu_2Sn(OAc)_2$	1.4×10^{-3}	43[b]
5	$(AcO)Bu_2SnOSnBu_2(OAc)$	1.4×10^{-3}	42[b]
6	$Sc(O_3SCF_3)_3$	4.9×10^{-5}	2[b]
7	$Sm(O_3SCF_3)_3$	2.0×10^{-3}	45[b]
8	$Yb(O_3SCF_3)_3$	8.7×10^{-4}	30[b]
9	$La(O_3SCF_3)_3$	1.1×10^{-4}	6[b]
10	$Bu_2Sn(OAc)_2$		79[c]
11	$Bi(O_3SCF_3)_3$		92[c]

[a] $mol^{-1}\ L^{-1}\ min^{-1}$.

[b] % *N*-hexyl *O*-octyl carbamate after 3 h at 122°C.

[c] % *N*-hexyl *O*-octyl carbamate after 2 h at 160°C.

Arrhenius activation energy E_a was 112±9 kJ mol^{-1} for bismuth trifluoromethanesulfonate and 121±9 kJ mol^{-1} for 1,3-diacetoxy-1,1,3,3-tetrabutyl-distannoxane. The value of E_a for the formation of *N*-octyl carbamate therefore indicates a highly energetic reaction which is sensitive to small changes in temperature. It is higher than those reported for carbamate deblocking reactions with more reactive blocking agents.[12]

Surprisingly, even though some catalysts for the addition of alcohols to isocyanates are usually also active in the transcarbamoylation reaction,[13] triphenylbismuth showed no activity at all. Bismuth trichloride was more active but revealed a lower activity than common organotin compounds such as dibutyltin diacetate or 1,3-diacetoxy-1,1,3,3-tetrabutyldistannoxane (see Table 1). Next, we turned to bismuth trifluoromethanesulfonate. It showed a higher activity than that of the usual organotin catalysts.[14] The rate constant of the reaction was calculated at 4.5×10^{-3} mol^{-1} L min^{-1} for the bismuth trifluoromethanesulfonate while a value of 1.4×10^{-3} mol^{-1} L^{-1} min^{-1} was recorded for both dibutyltin diacetate and 1,3-diacetoxy-1,1,3,3-tetrabutyldistannoxane. The higher reactivity of bismuth trifluoromethanesulfonate was also reflected in the yield of the reaction. After 2 hours at 160°C, the yield in *N*-hexyl *O*-*n*-octyl carbamate reached 92% with the bismuth compound while it was limited to 79% with dibutyltin acetate.

Moreover, bismuth trifluoromethanesulfonate turned out to be not only more active but also more selective than tin derivatives. While with oxime-derived carbamates and organotin catalysts no isocyanate could be detected in the transcarbamoylation with polyols,[13] the use of dibutyltin acetate and 1,3-diacetoxy-1,1,3,3-tetrabutyldistannoxane as catalysts led to the formation of some hexyl isocyanate, which was formed during the reaction in a yield which could go up to 15% at 160°C. The absence of volatile isocyanate which could escape during the transcarbamoylation reaction is thus another important improvement provided by bismuth trifluoromethane sulfonate. Encouraged by these good results, we turned to other triflates derived from scandium[15] and rare earths[16] which recently proved to be excellent Lewis acids with very interesting applications in catalysis. All of them were found to be active in our model transcarbamoylation reaction. Samarium triflate gave better results than ytterbium and lanthanum triflates, while scandium triflate, which is the 'harder' among these metallic esters, did not show very high catalytic properties. However none of them reached the excellent results obtained with bismuth trifluoromethanesulfonate.

The procedure for the kinetic experiments of transcarbamoylation was as follows. In a dry 2-necked 10 ml flask under nitrogen with a short path column, a receiver, and a septum, *N*-hexyl *O*-methyl carbamate (500 mg; 3.14 mmol) was added to a mixture of catalyst (1% mol, 3.14×10^{-2} mmol), *n*-octanol (409 mg, 3.14 mmol) and hexadecane (355 mg, 1.57 mmol). The solution was heated at 122°C (internal temperature) and aliquots analysed by GC on a capillary column.

In summary, bismuth trifluoromethanesulfonate was shown to be a very efficient catalyst in the transcarbamoylation reaction of *N*-alkyl *O*-alkyl carbamates. This compound was more active than common catalysts and also more selective; isocyanates were not detected during the reaction.

References

1. (a) Wicks, Z. *Progress Org. Coatings* **1975**, *3*, 73; (b) Wicks, Z.; Jones, F. N.; Pappas, S. P. *Organic Coatings*: *Science and Technology*; Wiley: New York, 1992; p. 204.
2. (a) Huang, Y.; Chu, G.; Nieh, M.; Jones, F. N. *J. Coatings Technol.* **1995**, *67*, 33; (b) Lucas, H. R.; Wu, K.-J. *J. Coatings Technol.* **1993**, *65*, 59; (c) Shaffer, M. W.; Potter, T. A.; Salek, M. M. *J. Polym. Mater. Sci. Eng.* **1994**, 112; (d) Blank, W. J. *J. Polym. Mater. Sci. Eng.* **1990**, 931; (e) Provder, T. *J. Coatings Technol.* **1989**, *61*, 33.
3. (a) Wada, M.; Takeichi, E.; Matsumoto, T. *Bull. Chem. Soc. Jpn.* **1991**, *69*, 990; (b) Le Roux, C.; Gaspard-Iloughmane, H.; Dubac, J. *Bull. Soc. Chim. Fr.* **1994**, *130*, 832; (c) Le Roux, C.; Gaspard-Iloughmane, H.; Dubac, J. *J. Org. Chem.* **1994**, *59*, 2238.
4. Le Roux, C.; Gaspard-Iloughmane, H.; Dubac, J.; Jaud, J.; Vignaux, P. *J. Org. Chem.* **1993**, *58*, 1835.
5. (a) Desmurs, J. R.; Labrouillère, M.; Le Roux, C.; Gaspard, H.; Laporterie, A.; Dubac, J. *Tetrahedron Lett.* **1997**, *38*, 8871; (b) Répichet, S.; Le Roux, C.; Dubac, J.; Desmurs, J.-R. *Eur. J. Org. Chem.* **1998**, 2743; (c) Répichet, S.; Le Roux, C.; Hernandez, P.; Dubac, J. *J. Org. Chem.* **1999**, *64*, 6479.
6. Garrigues, B.; Gonzaga, F.; Robert, H.; Dubac, J. *J. Org. Chem.* **1997**, *62*, 4880.

7. Laurent-Robert, H.; Garrigues, B.; Dubac, J. *Synlett* **2000**, 1160.
8. Orita, A.; Tanahashi, C.; Kakuda, A.; Otera, J. *Angew. Chem. Int. Ed.* **2000**, *39*, 2877.
9. Luo, S.-G.; Tan, H.-M.; Zhang, J.-G.; Wu, Y.-J.; Pei, F.-K.; Meng, X.-H. *J. Appl. Polym. Sci.* **1997**, *65*, 1217.
10. (a) Gitlitz, M. H.; Seshadri, S. R. Eur. Patent 810245 A1, 1997; *Chem. Abstr.* **1997**, *128*, 48612; (b) Yasuoka, Y.; Kume, M.; Hiraki, T.; Kato, K.; Haneishi, H.; Yamamoto, M. Eur. Patent 509437 A1, 1992; *Chem. Abstr.* **1993**, *118*, 82914; (c) Williams, T. US Patent 4701488, 1987; *Chem. Abstr.* **1988**, *108*, 206120.
11. (a) Pereyre, M.; Quintard, J. P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987; (b) Jousseaume, B.; Pereyre, M. In *Chemistry of Tin*; Smith, P. J., Ed., 2nd ed.; Blackie: Glasgow, 1998; p. 290; (c) Sato, T. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Oxford, 1995; Vol. 11, p. 355; (d) Otera, J. *Chem. Rev.* **1993**, *93*, 1449.
12. Muizebelt, W. J. *J. Coatings Technol.* **1985**, *57*, 43.
13. Seshadri, S. R.; Gitlitz, M.; Bossert, E. C. *Waterborne, High-Solids and Powder Coatings Symposium*, **1996**, 492.
14. Bernard, J.-M.; Jousseaume, B.; Laporte, C.; Toupance, T. PCT Int. Appl. WO 0231014, 2002; *Chem. Abstr.* **2002**, *136*, 325992.
15. Kobayashi, S. *Eur. J. Org. Chem.* **1999**, 15 and references cited therein.
16. Kobayashi, S. *Synlett* **1994**, 689 and references cited therein.