Available online at www.sciencedirect.com

ScienceDirect

Tetrahedron Letters 49 (2008) 699–702

Tetrahedron Letters

An imido-transfer reaction of aldehydes with *N*-sulfinylamines using vanadium and molybdenum oxochlorides as catalysts

Anton A. Zhizhin, Dmitry N. Zarubin *, Nikolai A. Ustynyuk

A. N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences, Vavilov Street 28, 119991 Moscow, Russia

Received 23 August 2007; revised 14 November 2007; accepted 21 November 2007

Abstract

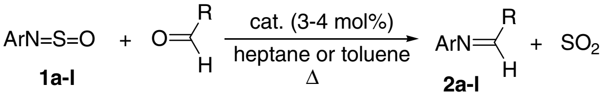
Vanadium and molybdenum oxochlorides were found to be efficient catalysts for imido-transfer between aldehydes and *N*-sulfinylamines.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Imidation; *N*-Sulfinylamine; Aldehyde; Azomethine; Vanadium; Molybdenum; Catalysis

The development of transition metal-mediated imido transfer reactions is an area of considerable interest. The aziridination and allylic amidation of alkenes,[1] transformation of phosphines into iminophosphoranes,[2] condensation of isocyanates into carbodiimides,[3] metathesis of imines[4] and carbodiimides[5] are well-studied examples. Schiff bases containing additional n-donor atoms represent one of the most important types of polydentate ligands in the coordination chemistry of transition and non-transition metals. Two synthetic procedures were proposed to prepare azomethines via catalytic imido-transfer reaction, (i) $MeReO_3$ catalysed the imidation of aldehydes by isocyanates as reported by Wang and Espenson,[6] and (ii) ruthenium catalysed imido-transfer reaction of $Ph_3P{=}NTs$[7a] or $PhI{=}NTs/PPh_3$[7b] with aldehydes as reported by Sain et al. Both are selective water-free reactions and in comparison with the classic acid-catalysed condensation of aldehydes with primary amines, they have the advantage of not requiring the use of azeotropic distillation or water-absorption for promoting the process. The former reaction is restricted by the scope of the starting substrates while the latter is inconvenient because chromatographic purification of the target azomethines from triphenylphosphine oxide formed as a co-product is necessary. It has been reported that *N*-sulfinylamines which are easily prepared by the reaction of primary amines with thionyl chloride[8] can also act as an imidating reagent in stoichiometric imido-deoxygenation reactions of aldehydes. However, the scope of *N*-sulfinylamines concerned is restricted to highly reactive polyfluorinated compounds only.[9]

Here we report that using cheap and commercially available vanadium and molybdenum oxochlorides $MOCl_3$ ($M = V$, Mo) and MoO_2Cl_2 as catalysts allows the imido-transfer reaction to be extended to a wide range of both *N*-sulfinylamines and aldehydes (Scheme 1, Table 1). We found that the catalytic reaction proceeds in aliphatic or aromatic hydrocarbon solvents under an argon atmosphere and affords aldimines in high yields. Analogous vanadium and molybdenum imidochlorides demonstrate comparable catalytic properties. The reaction proceeds at room temperature only for *N*-sulfinylamines and aldehydes having both



1a-l

2a-l

cat.: $MOCl_3$ (M= V, Mo), MoO_2Cl_2, $(2,4,6\text{-}Br_3C_6H_2N)_2Mo(OMes)_2$

Scheme 1.

---

[*] Corresponding author. Tel.: +7 499 1358861; fax: +7 499 1355085.
E-mail address: zaroubine@ineos.ac.ru (D.N. Zarubin).

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2007.11.131

Table 1
The azomethines **2a**–**l** prepared by vanadium or molybdenum-catalysed reaction of *N*-sulfinylamines with aldehydes

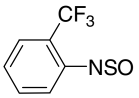
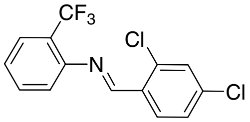
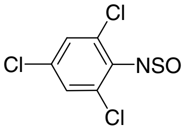
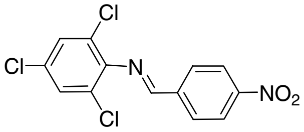
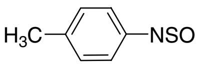
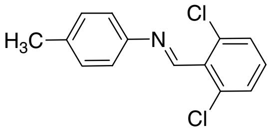
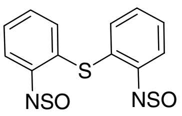
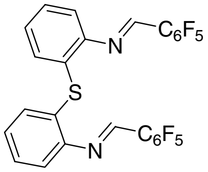
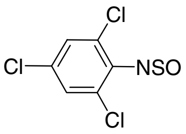
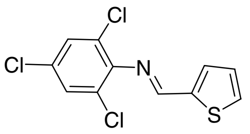
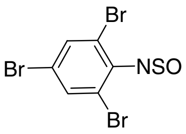
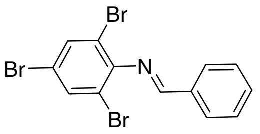
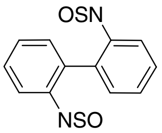
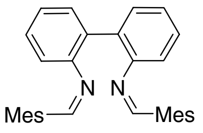
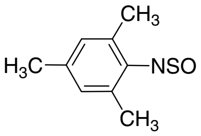
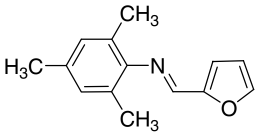
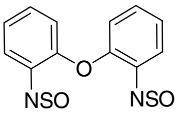
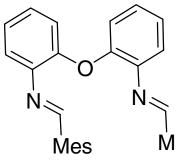
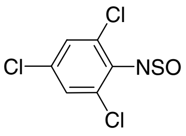
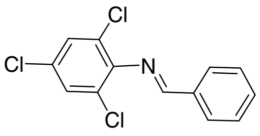
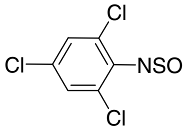
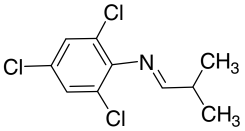
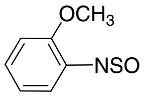
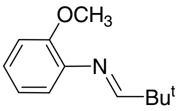
Entry	*N*-Sulfinylamine	Azomethine	Catalyst (mol %)	Conditions	Yield (%)
a			$VOCl_3$ (3)	Heptane, rt, 0.5 h	100[a] (84)[b]
b			$VOCl_3$ (3)	Heptane, reflux, 5 h	100 (98)
c			$VOCl_3$ (3.5)	Heptane, reflux, 4 h	91 (69)
d			$VOCl_3$ (3)	Heptane, reflux, 5 h	83 (75)
e			$VOCl_3$ (3)	Heptane, reflux, 28 h	81 (76)
f			MoO_2Cl_2 (3)	Toluene, reflux, 8 h	98 (77)
g			$MoOCl_3$ (3)	Toluene, reflux, 24 h	75 (73)
h			$MoOCl_3$ (3)	Toluene, reflux, 19 h	85 (72)
i			$MoOCl_3$ (3)	Toluene, reflux, 24 h	77 (74)
j			$(RN)_2Mo(OR')_2$[c] (4)	Heptane, reflux, 5 h	93 (89)

Table 1 (*continued*)

Entry	*N*-Sulfinylamine	Azomethine	Catalyst (mol %)	Conditions	Yield (%)
k			(RN)$_2$Mo(OR')$_2$^{c} (3)	Heptane, reflux, 5 h	64 (50)
l			(RN)$_2$Mo(OR')$_2$^{c} (3)	Toluene, reflux, 2.5 h	90 (86)

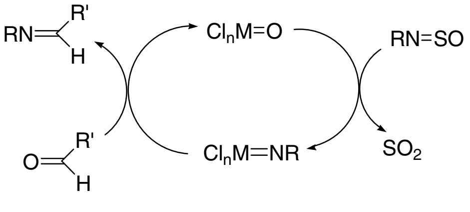
[a] Spectroscopically estimated.

[b] Isolated.

[c] R = 2,4,6-Br$_3$C$_6$H$_2$, R' = 2,4,6-Me$_3$C$_6$H$_2$.

good solubility in hydrocarbons and electron-withdrawing substituents (Table 1, entry a). In all the other cases studied, refluxing was necessary. Vanadium oxotrichloride works very well in aliphatic solvents with sterically unhindered substrates (Table 1, entries a–e). Molybdenum oxochlorides in toluene were preferred as catalysts for sterically hindered reagents, for example those containing mesityl or 2,4,6-tribromophenyl groups (Table 1, entries f–i). Neither vanadium nor molybdenum oxochlorides catalysed the reaction of *N*-sulfinylamines with aliphatic aldehydes. We also found that molybdenum imidoaroxide (2,4,6-Br$_3$C$_6$H$_2$N)$_2$Mo(OMes)$_2$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$) catalysed the imidation of branched aliphatic aldehydes to give aldimines (Table 1, entries k and l). It should be noted that (2,4,6-Br$_3$C$_6$H$_2$N)$_2$Mo(OMes)$_2$ is effective with both aliphatic and aromatic aldehydes. This method is especially useful for the synthesis of azomethines from poorly-nucleophilic primary amines which are difficult to access by classic acid-catalysed condensation of primary amines with aldehydes. To evaluate the effect of the catalyst, blank experiments were carried out under the same reaction conditions. 1-Sulfinylamino-2-(trifluoromethyl)benzene and 2,4-dichlorobenzaldehyde, 1,3,5-trimethyl-2-(sulfinylamino)benzene and 2-furaldehyde, and 1,3,5-trichloro-2-(sulfinylamino)benzene and 2-methylpropanal were mixed in pairs in the absence of catalysts. No aldimines were detected in all cases even after prolonged heating of the reaction mixtures.

The proposed catalytic cycle of the imido transfer process is shown in Scheme 2. For the reaction catalysed by metal oxochlorides the metathetical imido-deoxygenation of the oxochloride by *N*-sulfinylamine initially proceeds to afford the imido complex and sulfur dioxide as a coproduct. Then the complex undergoes the imido ligand exchange with the aldehyde to regenerate the starting oxochloride and release the target aldimine. The stoichiometric variants of the first[10] and the second stages[6,11] of this catalytic cycle are well documented in the literature. The same catalytic cycle is realised if imides are used as catalysts instead of oxides. In this case the catalytic cycle starts from the opposite position. The details of the mechanism are currently under investigation.



Scheme 2.

In summary, a novel water-free method for the synthesis of azomethines is presented. It is based on the imido-transfer reaction of aldehydes with *N*-sulfinylamines catalysed by vanadium or molybdenum oxochlorides. The advantages of this method are the easy availability of different *N*-sulfinyl derivatives of primary amines, cheap catalysts, high selectivity, simple operations and good yields. This method can be conveniently used for the preparation of a wide range of azomethines.

Acknowledgement

The research described in this publication was supported by the Russian Foundation for Basic Research (Grant 07-03-00939a).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.11.131.

References and notes

1. (a) Au, S.-M.; Huang, J.-S.; Yu, W.-Y.; Fung, W.-H.; Che, C. M. *J. Am. Chem. Soc.* **1999**, *121*, 9120–9132; (b) Cenini, S.; Tollari, S.; Penoni, A.; Cereda, C. *J. Mol. Catal. A: Chem.* **1999**, *137*, 135–146; (c) Liang, F. J.-L.; Huang, J. S.; Yu, X. Q.; Zhu, N.; Che, C.-M. *Chem. Eur. J.* **2002**, *8*, 1563–1572; (d) Leung, S. K.-Y.; Tsui, J.-S.; Huang, J.-S.; Che, C.-M.; Liang, J.-L.; Zhu, N. *J. Am. Chem. Soc.* **2005**, *127*, 16629–16640; and references therein.

2. (a) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186–193; (b) Leung, W.-H.; Wu, M.-C.; Lau, T.-C.; Wong, K.-Y. *Inorg. Chem.* **1995**, *34*, 4271–4274; (c) Leung, W.-H.; Hun, T. S. M.; Hou, H.-W.; Wong, K.-Y. *J. Chem. Soc., Dalton Trans.* **1997**, 237–244; (d) Smieja, J. A.; Borneman, M.; Kittilstved, K.; Edwards, D.; Borda, E. *Polyhedron* **2002**, *21*, 1889–1892.
3. Birdwhistell, K. R.; Boucher, T.; Ensminger, M.; Harris, S.; Johnson, M.; Toporek, S. *Organometallics* **1993**, *12*, 1023–1025.
4. (a) Cantrell, G. K.; Meyer, T. Y. *Chem. Commun.* **1997**, 1551–1552; (b) Cantrell, G. K.; Meyer, T. Y. *Organometallics* **1997**, *16*, 5381–5383; (c) Cantrell, G. K.; Meyer, T. Y. *J. Am. Chem. Soc.* **1998**, *120*, 8035–8042; (d) Burland, M. C.; Pontz, T. W.; Meyer, T. Y. *Organometallics* **2002**, *21*, 1933–1941; (e) Zuckerman, R. L.; Krska, S. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 751–761; (f) Bruno, J.-W.; Li, X. J. *Organometallics* **2000**, *19*, 4672–4674.
5. (a) Meisel, I.; Hertel, G.; Weiss, K. *J. Mol. Catal.* **1986**, *36*, 159–162; (b) Birdwhistell, K. R.; Lanza, J.; Pasos, J. *J. Organomet. Chem.* **1999**, *584*, 200–205; (c) Holand, A. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 9010–9011.
6. Wang, W.-D.; Espenson, J. H. *Organometallics* **1999**, *18*, 5170–5175.
7. (a) Jain, S. L.; Sharma, V. B.; Sain, B. *Tetrahedron Lett.* **2004**, *45*, 4341–4343; (b) Jain, S. L.; Sharma, V. B.; Sain, B. *J. Mol. Catal. A: Chem.* **2005**, *239*, 92–95.
8. (a) Michaelis, A. *Justus Liebigs Ann. Chem.* **1893**, *274*, 200–266; (b) Kresze, G.; Maschke, A.; Albrecht, R.; Bederke, K.; Patzschke, H. P.; Smalla, H.; Trede, A. *Angew. Chem.* **1962**, *74*, 135–144; (c) Meller, A.; Maringgele, W.; Fetzer, H. *Chem. Ber.* **1980**, *113*, 1950–1961.
9. (a) Li, A.; Zhu, S.-z.; Huang, Q.-c.; Liu, J.-s. *J. Fluor. Chem.* **1994**, *68*, 145–148; (b) Markovskii, L. N.; Solov'ev, A. V.; Kolesnik, N. P.; Shermolovich, ; Yu, G. *Russ. J. Org. Chem.* **1995**, *31*, 605–608; (c) Moiseev, S. V.; Goncharov, V. M.; Zatonsky, G. V.; Cherstkov, V. F.; Vasil'ev, N. V. *Mendeleev Commun.* **2006**, 184–186.
10. (a) La Monica, G.; Cenini, S. *Inorg. Chim. Acta* **1978**, *29*, 183–187; (b) Cenini, S.; Pizzotti, M. *Inorg. Chim. Acta* **1980**, *42*, 65–68; (c) Rufanov, K. A.; Zarubin, D. N.; Ustynyuk, N. A.; Gourevitch, D. N.; Sundermeyer, J.; Churakov, A. V.; Howard, J. A. K. *Polyhedron* **2001**, *20*, 379–385; (d) Zaroubine, D. N.; Holovko, D. S.; Ustynyuk, N. A. *Russ. Chem. Bull., Int. Ed.* **2002**, *51*, 1075–1076.
11. (a) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1978**, 579–580; (b) Schrock, R. R.; Rocklage, S. M. *J. Am. Chem. Soc.* **1980**, *102*, 7808–7809; (c) Jolly, M.; Mitchell, J. P.; Gibson, V. C. *J. Chem. Soc., Dalton. Trans.* **1992**, 1329–1330; (d) Moubaraki, B.; Murray, K. S.; Nichols, P. J.; Thomson, S.; West, B. O. *Polyhedron* **1994**, *13*, 485–495; (e) Royo, P.; Sánchez-Nieves, J. *J. Organomet. Chem.* **2000**, *597*, 61–68.