This article was downloaded by: [Duke University Libraries] On: 31 December 2014, At: 08:59 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

Calcined ZnCrCo₃-HTlc for the oxidation of benzyl amines to schiff bases⁺

B. M. Choudary^a, N. Narender^a & V. Bhuma^a

^a Homogeneous Catalysis Discipline Indian Institute of Chemical Technology, Hyderabad, 500007, INDIA Published online: 21 Nov 2007.

To cite this article: B. M. Choudary , N. Narender & V. Bhuma (1996) Calcined ZnCrCo₃-HTIc for the oxidation of benzyl amines to schiff bases⁺, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 26:4, 631-635, DOI: <u>10.1080/00397919608086735</u>

To link to this article: http://dx.doi.org/10.1080/00397919608086735

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any

losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <u>http://www.tandfonline.com/page/terms-and-conditions</u>

CALCINED ZnCrCO₃-HTIc FOR THE OXIDATION OF BENZYL AMINES TO SCHIFF BASES⁺

B.M. Choudary*, N. Narender and V. Bhuma

Homogeneous Catalysis Discipline Indian Institute of Chemical Technology Hyderabad 500007, INDIA

ABSTRACT Oxidation of benzylamines to Schiff bases has been carried out using a mixed oxide catalyst obtained by the calcination of ZnCrCO₃-HTlc which is a member of the anionic clay family.

Transition metal catalysed oxidations of amines are of great biological and synthetic importance. These reactions display a rich diversity in mechanisms and may lead to the formation of either carbonyl compounds, amides, nitriles or Schiff bases. In the course of our project directed towards the applicability of hydrotalcites for organic synthesis, we have already reported interesting results on the utility of calcined ZnCrCO₃-HTlc for the hydroperoxidation of aralkanes¹ and oxidation of alkyl and benzyl pyridines to pyridyl ketones². The latter reaction shows the efficacy of the catalyst in the oxidation of acid sensitive nitrogen

IICT Communication No.: 3492 *To whom correspondence should be addressed containing organic substrates. In this report we describe the use of calcined ZnCrCO₃-HTlc, a solid catalyst in conjunction with anhydrous TBHP for the oxidation of benzylamines to Schiff bases.

The oxidation of benzylamines catalysed by using calcined ZnCrCO₃-HTlc³, to form the corresponding Schiff bases with excellent yields and high selectivities is shown in Table 1. The methodology is found to be equally efficient with both primary and secondary benzylamines (Scheme 1&2). Electron withdrawing substituents in the benzene ring enhance the yield of the product in comparison to electron donating substituents which give lesser yields (entries 2&3).

The salient feature of the present catalytic methodology is the selective oxidation of N-phenethyl benzylamine to the corresponding Schiff base with 90% selectivity (entry 7). Similarly 4-methyl benzylamine affords the corresponding Schiff base without the oxidation of the facile methyl group (entry 4) although the catalyst is found to be reactive with toluene, under similar conditions to give benzyl hydroperoxide¹ Tetrahydroisoquinoline yields 3,4-dihydroisoquinoline which is an important precursor of nitrogen containing natural products (entry 8).





Table 1. Oxidation of benzylamines to schiff bases using calcined ZnCrCO₃ - HTIc

Entry	Substrate	Product	Product a conv. (%)	Schiff base sel (%)b
	R-CI NH2	R-CI N CH-R		
1	R = H		90	98
2	R = p - OMe		60	90
3	R = p-Cl		80	92
4	R = p - Me		70	96
5			60	58 ^c
6			96	98
7			67	90
8			88	90
9			50	80

a - Based on starting material recovered

b - Calculated based on isolated yields

c - 42% of acetophenone was recovered

Increase in the reaction temperature results in the formation of byproducts thus, reducing the selectivity for the Schiff base obtained.

Thus, the present catalytic methodology is very mild and involves the use of a heterogeneous catalyst which is reusable in comparison with the expensive ruthenium⁴ and other reported methodologies⁵.

Experimental

Preparation of ZnCrCO₃-HTlc:-

The ZnCrCO₃-HTlc was prepared by the procedure reported by *Reichle et al*³. The catalyst was calcined at 723 K for 1 hr.

General procedure for the oxidation of primary and secondary amines

A 100 ml round bottomed flask was charged with 250 mg of calcined $ZnCrCO_3$ -HTlc, 4 mmols of substrate in dry dichloromethane under N₂ atmosphere and initially stirred for 1/2 hr. Then, 3.5 ml(8mmol) of TBHP was added and the reaction contents allowed to stir for 36 hrs at room temperature. The progress of the reaction was monitered by TLC. After the completion of the reaction, the catalyst was filtered, washed with dichloromethane and the filtrate was concentrated under reduced pressure. The products were purified by column chromatography. The products were confirmed by ¹H NMR and Mass spectra.

Acknowledgements

We thank CSIR for financial support to N. Narender and V. Bhuma.

References

- 1. Choudary, B.M., Narender, N. and Bhuma, V. Synlett. 1994, 8, 641
- 2. Choudary, B.M., Bhuma, V. and Narender, N. (Communicated).
- Reichle, W.T. J. Catal. 1985, 94, 547. The catalyst was calcined at 723 K for l hr in oxygen atmosphere.
- (a) Murahashi, S.I., Naoto, T. and Taki, H. J. Chem. Soc., Chem. Commun. 1985, 613.
 - (b) Muller, P. and Gilbert, D.M. Tetrahedron. 1988, 44, 7171.
- 5. (a) Bacon, R.G.R. and Stewart, D. J. Chem. Soc. (C).1966, 1384.
 (b) Nishinaga, A., Yamazaki, S. and Matsuura, T. Tetrahedron Lett. 1988, 29, 4115.
 - (c) Tollari, S., Bruni, S., Bianchi, C.L., Rainoni, M. and Porta, F. J. Mol. Catal. 1993, 83, 311.
 - (d) Nakayama, K., Hamamoto, M., Nishiyama, Y. and Ishii, Y. Chemistry Lett. 1993, 1699.

(Received in the UK 20 July 1995)