This article was downloaded by: [Moskow State Univ Bibliote] On: 11 December 2013, At: 06:30 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: <u>http://www.tandfonline.com/loi/lsyc20</u>

Iodobenzene Dichloride -An Efficient Reagent for Preparation of Nitrile Oxides from Aldoximes

A S Radhakrishna ^a , K Sivaprakash ^a & B B Singh ^a

^a R&D Centre, Reckitt & Colman of India Limited, Plot 176, SIPCOT Industrial Complex, Hosur, 635 126, Tamil Nadu, India Published online: 23 Sep 2006.

To cite this article: A S Radhakrishna , K Sivaprakash & B B Singh (1991) Iodobenzene Dichloride - An Efficient Reagent for Preparation of Nitrile Oxides from Aldoximes, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 21:15-16, 1625-1629, DOI: <u>10.1080/00397919108021062</u>

To link to this article: http://dx.doi.org/10.1080/00397919108021062

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>

IODOBENZENE DICHLORIDE ~ AN EFFICIENT REAGENT FOR PREPARATION OF NITRILE OXIDES FROM ALDOXIMES

A S Radhakrishna, K Sivaprakash and B B Singh*

- R&D Centre, Reckitt & Colman of India Limited, Plot 176, SIPCOT Industrial Complex, Hosur-635 126, Tamil Nadu, India
- Summary : Reaction of aldoximes with iodobenzene dichloride leads to formation of corresponding nitrile oxides in good yields in a single pot reaction.

Nitrile oxides form an important class of reactive intermediates because of their ability to undergo 1,3-dipolar additions giving heterocyclic compounds, especially isoxazolines isoxazoles. Most of the nitrile oxides are too reactive and isolated and they undergo dimerization if not reacted to be with appropriate substrates. However, in the cases in situ where the aldoxime group is sterically hindered, the resulting have been isolated, characterized and reacted nitrile oxides substrates² of Isoxazolines and isoxazoles, with variety which readily converted to polyfunctional derivatives are and 1,3-diketones, such as enamino ketones. amino ketones class receiving much attention as an important of are intermediates for studies directed towards natural product synthesis³ The different methods used for preparing nitrile involve dehydrohalogenation of α -halo aldoximes, the oxides

1625

oxidative dehydrogenation of aldoximes, the dehydration of primary nitro compounds. and the dehydrohalogenation of halides^{1,2} hydroximinoyl oxidative dehydrogenation А few methods of aldoximes have been reported such as lead tetraacetate, alkali hypohalite, N-bromosuccinimide in D.M.F. followed by base treatment, chloramine-T, 1-chlorobenzotriazole, Hypervalent iodine compounds have been extensively etc. studied in recent for bringing about years various transformations.

We report here a simple one pot conversion of aldoximes with iodobenzene dichloride. nitrile oxides by reaction to The treatment of several aldoximes in chloroform with iodobenzene dichloride in the presence of pyridine or triethyl the corresponding nitrile oxides. amine gave The nitrile oxides were identified by their IR spectra but slowly dimerised or decomposed on standing or heating. Further, the nitrile oxides so generated, have been reacted insitu with an olefinic compound to get the 1,3-dipolar addition product in good yields (Scheme 1; Table).



IODOBENZENE DICHLORIDE



TABLE



SCHEME 2

The present procedure has also been used for intramolecular nitrile oxide cyclo-addition reaction. For example, 2-allyloxybenzaldoxime afforded the corresponding isoxazoline by treatment with iodobenzene dichloride in moderate yields (Scheme 2; Table).

Experimental

2 equivalents of pyridine/triethylamine as base and chloroform as solvent were used in all the reactions. Products were characterised by comparison of (IR, $^{1}\text{H-NMR}$ and m.p.), with those reported in the literature. All yields refer to isolated yields after purification by column chromatography on silica gel.

3-(4-Methoxy)phenyl-4-(3,4-methylenedioxy)benzyl-4,5-dihydroisoxazole (Entry 4, Table) Typical procedure :

To a stirred solution of 4-methoxybenzaldoxime (1.51g, 0.01M) in chloroform (40m1), pyridine (1.58g, 0.02M) is added and the mixture cooled in water at room temperature. Iodobenzene dichloride (2.74g, 0.01M) is added in portions during 2 min. Reaction mixture stirred at room temperature 1-Allyl-3,4-methylenedioxybenzene (1.62g, 0.01M) for ł h,

IODOBENZENE DICHLORIDE

is now added and the reaction mixture heated under reflux The cooled reaction mixture was washed successively for 5 h. with water, 5% ag. HCl solution and water. Organic laver briefly dried over anhydrous sodium sulfate and solvents distilled off under reduced pressure. The residue is subjected to column chromatography (hexane-chloroform) and the pure isolated. Yield : 1.38g (65%) m.p. 83-85°C. product is

References

- 1. Grundman, C., Synthesis, 1970, 344.
- Ranganathan, S., Singh, B.B., and Panda, C.S., Tetrahedron Lett., 1970, 1225, and references contained therein.
- 3.(a) Kozikowski, A.P., Acc.Chem.Res., 1984, 17, 410.
 - (b) Baraldi, P.G., Barco, A., Benetti, S., Pollini, G.P., Simoni, D., Synthesis, 1987, 857.
- 4. Just, G., Dahl, K., Tetrahedron Lett., 1968, 24, 5251.
- Grundman, C., and Dean, J.M., J.Org.Chem., 1965, 30, 2809.
- Grundman, C., and Richter, R., J.Org.Chem., 1968, 33, 476.
- Hassner, A., and Lokanatha Rao, K.M., Synthesis, 1989, 57.
- Kim, J.N., and Ryu, K.R., Synthetic Commun., 1990, 20, 1373-1377.

9. Varvoglis, A., Synthesis, 1984, 709. (Received in UK 23 April, 1991)