This article was downloaded by: [Stony Brook University] On: 03 November 2014, At: 02:53 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>

Silica Supported Ferric Nitrate Nonahydrate: Selective Oxidation of Benzoins Under Mild Conditions

Aniruddha M. Paul^a, Amit C. Khandekar^a & M. A. Shenoy^a ^a Applied Chemistry Division, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai, India Published online: 17 Aug 2006.

To cite this article: Aniruddha M. Paul, Amit C. Khandekar & M. A. Shenoy (2003) Silica Supported Ferric Nitrate Nonahydrate: Selective Oxidation of Benzoins Under Mild Conditions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 33:15, 2581-2584, DOI: <u>10.1081/SCC-120021976</u>

To link to this article: <u>http://dx.doi.org/10.1081/SCC-120021976</u>

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 http://www.tandfonline.com/page/terms-and-conditions



MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

©2003 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

SYNTHETIC COMMUNICATIONS[®] Vol. 33, No. 15, pp. 2581–2584, 2003

Silica Supported Ferric Nitrate Nonahydrate: Selective Oxidation of Benzoins Under Mild Conditions

Aniruddha M. Paul, Amit C. Khandekar, and M. A. Shenoy*

Applied Chemistry Division, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai, India

ABSTRACT

Benzils are selectively obtained in high yields by the oxidation of benzoins under mild reaction conditions using silica supported ferric nitrate nonahydrate.

Key Words: Benzoins; Silfen; Oxidation; Benzils.

2581

DOI: 10.1081/SCC-120021976 Copyright © 2003 by Marcel Dekker, Inc. 0039-7911 (Print); 1532-2432 (Online) www.dekker.com

^{*}Correspondence: M. A. Shenoy, Applied Chemistry Division, Institute of Chemical Technology, University of Mumbai, Nathalal Parikh Marg., Matunga, Mumbai 400019, India; Fax: 91-22-4145619; E-mail: amp_bmk@ yahoo.co.in.

NY A

©2003 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

2582

Paul, Khandekar, and Shenoy

Table 1. Optimization of molar ratio of ferric nitrate to benzoin $(R_1 = C_6H_5, R_2 = C_6H_5)$.

Molar ratio Fe(NO ₃) ₃ ·9H ₂ O:benzoin	Reaction time (h)	Yield ^a (%)	
1:7	5	72	
1:6	5	79	
1:5	5	83	
1:4	5	89	
1:3	3	93	
1:2	3	95	
1:1	3	94	

^aRefers to pure isolated products.

The synthetic utility of supported reagents for a wide range of organic reactions has been explored earlier in our laboratory.^[1] In continuation of our progressive investigation on supported reagents, we now report the selective oxidation of various symmetrical and unsymmetrical benzoins to the corresponding benzils using silica supported ferric nitrate nonahydrate (silfen). The reagent, silfen was prepared by simply cogrinding silica gel (230–400 mesh) with ferric nitrate nonahydrate in the ratio 4:1 (w/w) in an agate mortar and used without prior activation.

For the purpose of optimization of molar ratio of ferric nitrate nonahydrate to benzoin, we carried out the reaction by varying the molar ratio from 1:1 to 1:7. The optimum ratio was found to be 1:3. Even for the molar ratio of 1:7, a moderate yield of 72% was obtained (Table 1). It should be noted that the quantity of ferric nitrate nonahydrate required in this method is much less as compared to the reported methods, e.g., the ratio is found to be 1:2 in case of clayfen^[2] and 2.5:1 in case of ferric nitrate nonahydrate^[3] for the same reaction.

In conclusion, the decrease in the amount of ferric nitrate nonahydrate results in considerable reduction of NO_x evolution along with improved safety and handling. In addition to this, our reagent is cheap and easy to prepare, even in large scale using a jar mill or a ball mill. Our method, therefore, offers a clear advantage over the earlier reported methods.

EXPERIMENTAL

The starting benzoins were prepared as per the reported procedures.^[4,5] Melting points are uncorrected and taken in open capillaries MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

2583

©2003 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.



Table 2. Oxidation of benzoins using silica supported ferric nitrate nonahydrate.

Entry no.	R_1	R_2	Time (h)	Yield ^a (%)	M.p. found (°C)	M.p. reported (°C)
1	Ph	Ph	3	93	94–95	93
2	p-MeC ₆ H ₄	p-MeC ₆ H ₄	3	95	98-100	102-103
3	C_6H_5	p-ClC ₆ H ₄	3	93	76–77	73
4	$p-ClC_6H_4$	C_6H_5	3	93	76–77	73
5	p-BrC ₆ H ₄	C_6H_5	3	92	87-88	88-89
6	C_6H_5	p-BrC ₆ H ₄	3	92	86-88	88-89
7	<i>p</i> -MeOC ₆ H ₄	C_6H_5	3	82	60-61	61-62
8	$o-ClC_6H_4$	<i>p</i> -MeOC ₆ H ₄	3	96	105-106	103-104
9	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -MeOC ₆ H ₄	4	92	128–130	131-132

^aRefers to pure isolated products.

The products obtained showed satisfactory physical and spectral data.

on an Oswal precision melting point apparatus. Infrared spectra was recorded as KBr pellets on a Jasco FTIR 410 E spectrophotometer, ¹H NMR spectra was recorded at 500 MHz using CDC1₃/TMS on a Bruker X-500 spectrometer.

General Procedure for Oxidation of Benzoins

Benzoin (5 mmo1) and SiO₂-Fe(NO₃)₃·9H₂O (3.4 g, 1.7 mmo1) are added to ethylene dichloride (20 mL) and the mixture is refluxed for 3 to 4 h (Sch. 1). The completion of reaction was monitored by TLC (hexane–ethyl acetate, 9:1). The product is isolated by desorption with hot ethylene dichloride. The excess solvent is removed by distillation. The product is dissolved in minimum amount of ether and passed through a short silica column for purification. The products (Table 2) were characterized by their melting points,^[4,6] IR and ¹H NMR. MA.

©2003 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

2584

Paul, Khandekar, and Shenoy

ACKNOWLEDGMENT

The authors are thankful to AICTE, New Delhi and BRNS for financial assistance. Thanks are also due to Prof. S. D. Samant and late Dr. B. M. Khadilkar for their valuable suggestions.

REFERENCES

- 1. (a) Khadilkar, B.M.; Borkar, S.D. Silica gel supported ferric nitrate: a convenient oxidizing agent. Synth. Commun. 1998, 28, 207–212; (b) Khadilkar, B.M.; Borkar, S.D. Synthesis of benzophenones using silica gel supported Lewis acid catalyst. Tetrahedron Lett. 1997, 38, 1641-1642; (c) Khadilkar, B.M.; Borkar, S.D. Environmentally clean synthesis of diphenylmetane using silica supported ZnCl₂ and FeCl₃. J. Chem. Technol. Biotechnol. 1998, 71, 209-212; (d) Khadilkar, B.M.; Bendale, P.M. Microwave promoted regeneration of carbonyl compounds from oximes using silica supported chromium trioxide. Tetrahedron Lett. 1998, 39, 5867-5868; (e) Khadilkar, B.M.; Madyar, V.R. Totally selective dry microwave assisted amide synthesis by hydration of nitrile using silica supported MnO_2 reagent. Synth. Commun. 2002, 32, 1731–1734; (f) Khadilkar, B.M.; Khandekar, A.C.; Paul, A.M. Silica supported manganese dioxide: an efficient reagent for oxidation of benzoins. Synth. Commun. 2002, 32, 2931-2935.
- 2. Cornelis, A.; Laszlo, P. Clay-supported copper(II) and iron(III) nitrates: novel multi-purpose reagents for organic synthesis. Synthesis **1985**, 909–918.
- 3. Zhao, Y.-W.; Wang, Y.-L. Solvent-free oxidation of benzoins using Fe(NO₃)₃·9H₂O the oxidant. J. Chem. Res. (S) **2001**, 70–71.
- 4. Richard, T.A.; Fuson, R.C. A new synthesis of mixed benzoins. J. Amer. Chem. Soc. **1936**, *58*, 1295–1296.
- Ide, S.W.; Buck, J.S. The synthesis of benzoins. In Organic Reactions; John Wiley and Sons: NewYork, 1948, Vol. IV, 269–304.
- Mckillop, A.; Swann, B.P.; Ford, M.E.; Taylor, E.C. Thallium in organic synthesis. XXXVIII. Oxidation of chalcones, deoxybenzoins, and benzoins with thallium(III) nitrate (TTN). J. Amer. Chem. Soc. 1973, 95, 3641–3645.

Received in the Netherlands November 11, 2002