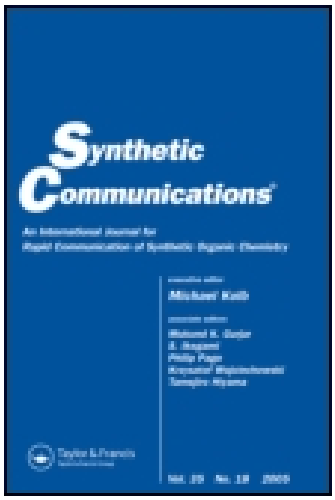

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

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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: 10.1081/SCC-120021976

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

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

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

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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.

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DOI: 10.1081/SCC-120021976 0039-7911 (Print); 1532-2432 (Online)

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

Molar ratio $Fe(NO_3)_3 \cdot 9H_2O$: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

[a]Refers to pure isolated products.

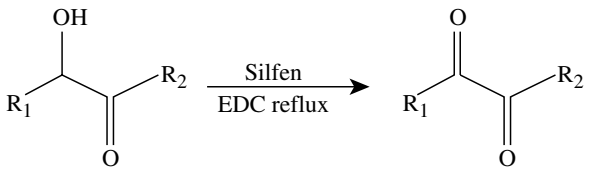
The synthetic utility of supported reagents for a wide range of organic reactions has been explored earlier in our laboratory.[1] In continuation of our progressive investigation on supported reagents, we now report the selective oxidation of various symmetrical and unsymmetrical benzoins to the corresponding 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



Scheme 1.

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_6H_4	*p*-MeC_6H_4	3	95	98–100	102–103
3	C_6H_5	*p*-ClC_6H_4	3	93	76–77	73
4	*p*-ClC_6H_4	C_6H_5	3	93	76–77	73
5	*p*-BrC_6H_4	C_6H_5	3	92	87–88	88–89
6	C_6H_5	*p*-BrC_6H_4	3	92	86–88	88–89
7	*p*-$MeOC_6H_4$	C_6H_5	3	82	60–61	61–62
8	*o*-ClC_6H_4	*p*-$MeOC_6H_4$	3	96	105–106	103–104
9	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	4	92	128–130	131–132

[a]Refers 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, ^{1}H NMR spectra was recorded at 500 MHz using $CDC1_3$/TMS on a Bruker X-500 spectrometer.

General Procedure for Oxidation of Benzoins

Benzoin (5 mmol) and SiO_2-$Fe(NO_3)_3 \cdot 9H_2O$ (3.4 g, 1.7 mmol) 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 ^{1}H NMR.

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.

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Received in the Netherlands November 11, 2002