

Solvent-free oxidation of benzoinz using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the oxidant[†]

Yue-Wei Zhao and Yu-Lu Wang*

School of Chemistry and Environmental Science, Henan Normal University

The Key Laboratory of Environmental Science and Technology of High Education of Henan Province, Xinxiang, 453002, Henan, P. R. China

Benzoinz are oxidised to benzilz using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the oxidant under solvent-free condition by heating in an oven or microwave irradiation.

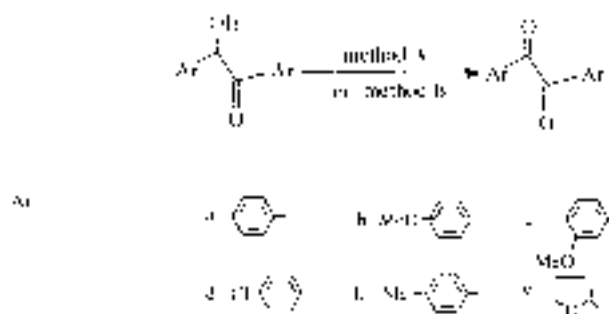
Keywords: solvent free oxidation, benzoinz, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

Oxidation of benzoinz is one of the important routes of the preparation of benzilz. It has been reported that benzoinz can be oxidised to benzilz by nitrosnitric acid, CuSO_4/Py , $\text{Fe}(\text{CN})_6^{3-}/\text{OH}^-$ and $\text{Bi}_2\text{O}_3/\text{H}^+$ in water solvent^{1–5} or by $\text{Ph}_3\text{PBr}_2/\text{MeCN}$ ⁶, $\text{DMSO}/(\text{COCl}_2)_2/\text{CH}_2\text{Cl}_2$ ⁷, $\text{PhCH}_2^+\text{NEtBr}_3/\text{MeCN}$ ⁸, NBS/CCl_4 ⁹, $\text{Clayfen}/n\text{-C}_6\text{H}_{14}$ ¹⁰, Bu_2SnO and $\text{Bu}_2\text{Sn}(\text{OMe})_2$ ¹¹, $\text{Ti}(\text{OPr-i})$ ¹² and $(\text{CH}_3)_2\text{NHCrO}_3\text{Cl}/\text{SiO}_2$ ¹³ in organic solvent. However, most of the processes mentioned above suffer from drawbacks such as extended reaction times, tedious purification and undesirable side products. Consequently, easy, rapid, convenient and environmentally benign protocols for the oxidation of benzoinz are required.

Microwave irradiation has been successfully applied in organic synthesis. Recently, reaction facilitated by microwaves under solvent-free condition have attracted more attention because of their enhanced selectivity, milder reaction conditions and associated ease of manipulation. Therefore microwave-assisted reactions for oxidation of benzoinz^{14, 15} are popular.

Hydrated ferric nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, is an excellent oxidant,^{10, 16–18} and has also been used as dehydrogenating agent.¹⁹ In this paper, we report two new methods of preparation of benzilz under solvent-free condition with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the oxidant. A series of benzoinz undergo rapid oxidation with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to afford vicinal diketones, showing that $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is a useful oxidant for these reactions. The benzilz that were prepared are listed in Table 1.

We found that $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ can oxidise benzoinz to benzilz in 15–20 minutes as long as certain temperatures are used (method A). Here, we optimised the reaction temperature at 100°C (over 100°C the resulting products would be difficult to filter and below 100°C the reaction time would be longer). However, under the microwave condition, the reaction time is shortened to 0.5–1 minute (method B). Thus it can be seen that



Scheme 1

the reaction rate was accelerated by microwave irradiation. The yields of benzilz are good under both two conditions.

We find the reaction of oxidation failed to proceed when $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was replaced with $\text{Fe}_2(\text{SO}_4)_3$ or $\text{K}_3\text{Fe}(\text{CN})_6$.

Compared with the reaction method using the clay-supported Iron (III) nitrate (clayfen)^{10,16} as the oxidant, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was directly used as the oxidant in our method. This resulted in a greater ease and simplification of the oxidative reaction. Furthermore, the reaction time was shortened dramatically and the strict procedures with potential hazard and extended work-up and preparation were avoided. The stability of the oxidant was taken into consideration.

Experimental

Melting points were determined with a Kofler micro melting point apparatus and were uncorrected. The reactions were carried out in a common oven or in a Galanz Cambi-Grill microwave oven (750 W) at minimal power level. General procedure for the synthesis of benzilz 2a–2f by methods A, B are described below. All the products were

Table 1 Prepared benzilz by the oxidation of benzoinz with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the oxidant

Entry	Method A		Method B		m.p./°C	
	Reaction times/min	Yields/%	Reaction times/min	Yields/%	Found	Reported
2a	15	95	0.5	93	92–94	94–96 ²⁰
2b	20	91	1.0	92	130–134	132–134 ²⁰
2c	15	93	0.5	95	80–82	83 ²²
2d	20	90	1.0	94	193–195	195–197 ²⁰
2e	15	94	0.5	95	102–104	101–104 ²⁰
2f	20	92	1.0	90	160–163	162–164 ²¹

* To receive any correspondence. Email: hnsdyj@public.xxptt.ha.cn

[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

characterised by comparing the melting point of the authentic samples.^{20,21}

Method A: Benzoin (1 mmol) and Fe(NO₃)₃·9H₂O (1 g) was mixed thoroughly and then put into an oven which was kept at 100°C for 15–20 minutes till the colour of the mixture changed to red-brown. Acetone (10m) was added to the crude mixture, then mixed thoroughly. After that, 30 ml of cold water was added and faint yellow products were precipitated. The products was isolated by filtration, recrystallised with methanol, the products were dried under vacuum.

Method B: Benzoin (1 mmol) and Fe(NO₃)₃·9H₂O (1 g) was mixed thoroughly and then irradiated in a microwave oven for 0.5~1 min. The later steps in the procedure were the same as in method A.

Received 1 October 2000; accepted 15 November 2000
Paper 00/533

References

- H.T. Clark and E.E. Dreger, *Org. Syn. Coll.*, 1941, **1**, 87.
- W. Rigby, *J. Chem. Soc.*, 1951, 793.
- L.F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, 1967, **1**, 734.
- R.A. Ei-Zaru and A. Jarrara, *A. Chem. Ind.*, 1977, 741.
- S. Rajan, K. Nagarajan, V. Jagannadhom and D. Ramesh, *Ind. J. Chem.*, 1979, **17B**, 80.
- T.L. Ho, *Synthesis*, 1972, 697.
- A.J. Mancuso, D.S. Brownfain and D. Swern, *J. Org. Chem.*, 1979, **44**, 4148.
- X.-S. Ding, G.-B. Liu, Z. Teng and W. Xu, *Youji Huaxue*, 1990, **10**, 366.
- M.-Z. Pu, *Huaxue Yu Nianhe*, 1994, **2**, 78.
- A. Conelis, P. Laszlo, *Synthesis*, 1985, 909.
- A.G. Davies and J.A. Hawari, *J. Chem. Soc., Perkin Trans I*, 1983, 875.
- B.-L. Lou and L.-X. Dai, *Youji Huaxue*, 1990, **10**, 357.
- G.-S. Zhang, Q.-Z. Shi, M.-F. Chen, K. Cai, *Hecheng Huaxue*, 1997, **2** (5), 218.
- H.-Z. Li, T.-S. Li, Tao Yu, J.-T. Li and Hong Chu, *Youji Huaxue*, 1998, **18**, 180.
- Alok Kumar Mitra, Aparna De and Nilay Karchaudhuri, *J. Chem. Res. (S)*, 1999, 246.
- A. Cornelis and P. Laszlo, *Synthesis*, 1980, 849.
- T. Nishiguchi and F. Asano, *Tetrahedron Lett.*, 1988, **29**(48), 6265.
- T. Nishiguchi and F. Asano, *J. Org. Chem.*, 1989, **54**, 1531.
- C.-L. Wang, Y.-L. Wang, X.-Y. Wang, X.-X. Wang and J.-P. Li, *J. Chin. Chem. Soc.*, 1999, **46**, 577.
- A. McKillop, B.P. Swann, M.E. Ford and E.C. Taylor, *J. Am. Chem. Soc.*, 1973, **95**, 3641.
- G.-S. Zhang, Q.-Z. Shi, M.-F. Chen and K. Cai, *Synth. Commun.*, 1997, **27**, 953, 3691.
- Beilsteins *Handbuch der organischen Chemie*, Band 8, Verlag-Springer, Berlin, 1925.