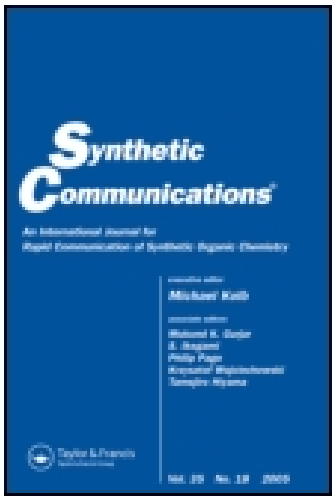

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REGENERATION OF KETONES FROM OXIMES IN DRY MEDIA UNDER MICROWAVE IRRADIATION

Jian-Feng Zhou [a] , Shu-Jiang Tu [b] & Jun-Cai Feng [c]

[a] Department of Chemistry , Huaiyin Normal College , Huaiyin, 223001, China

[b] Department of Chemistry , Xuzhou Normal University , Xuzhou, 221009, China

[c] Department of Chemistry , Nanjing University , Nanjing, 210093, China

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REGENERATION OF KETONES FROM OXIMES IN DRY MEDIA UNDER MICROWAVE IRRADIATION

Jian-Feng Zhou,[1] Shu-Jiang Tu,[2] and Jun-Cai Feng[3,*]

[1]Department of Chemistry,
Huaiyin Normal College, Huaiyin 223001, China
[2]Department of Chemistry,
Xuzhou Normal University, Xuzhou 221009, China
[3]Department of Chemistry,
Nanjing University, Nanjing 210093, China

ABSTRACT

Regeneration of ketones from oximes have been achieved using $HCOOH/SiO_2$ as solid support catalyst in dry media under microwave irradiation with 86 ~ 94% yield.

Oximes are extensively employed for characterization and purification of carbonyl compounds as well as in the preparation of amides.[1] Oximes can be prepared from carbonyl and non-carbonyl compounds (i.e. Barton reaction[2–3] etc.); therefore, deoximation of such oximes provides an alternative method for the synthesis of carbonyl compounds. In recent years cleavage of oximes to regenerate the parent carbonyl compounds has received much attention. Owing to the relative hydrolytic stability of oximes, a wide variety of deoximation reagents have been developed such

*Corresponding author.

as chromium trioxide-silica gel[4] and Ni(II)-complex catalyst[5]. However, these methods were performed in liquid phase and require stoichiometric or excess amounts of organic solvents. In some cases, reaction time is long (12 ~ 94 h) and the yield obtained very low.[6]

Microwave irradiation in organic synthesis is a useful technique. Dry media using microwave heating have attracted much attention.[7] A number of deoximation methods has been developed in dry media under microwave irradiation, such as silica supported ammonium persulfate,[8] silica supported sodium periodate,[9] pyridinium chloro-chromate[10] and clayfen.[11,12] In our laboratory, $HCOOH/SiO_2$ was used as a solid support catalyst for synthesis of nitriles[13] in dry media under microwave irradiation. $HCOOH/SiO_2$ was also used for synthesis of amides from ketones and hydroxylamine[14] in dry media under microwave irradiation, but further investigation revealed that most ketones cannot be converted to amides under these conditions. We found that the deoximation of ketoximes using $HCOOH/SiO_2$ as solid support catalyst in dry media under microwave irradiation was easy. Here we report a new and efficient method to regenerate ketones from oximes in dry media under microwave irradiation. The reactions are generally complete in 2–4 min with excellent yield.

The results obtained are shown in Table 1.

EXPERIMENTAL

All reagents were commercially available and used without further purification. $HCOOH/SiO_2$ was prepared from literature procedure.[14] Melting points were determined in open capillaries and uncorrected. IR spectra were recorded on a Nicolet FT-IR 5DX instrument. The reactions were carried out under atmospheric pressure with a modified commercial microwave oven (Sanle WP650D 650 W). All oximes were prepared by the standard procedures from commercially available ketones.

GENERAL PROCEDURE

Oxime (10 mmol) and $HCOOH/SiO_2$ (5 g) were thoroughly mixed in a flask (50 ml), connected to refluxing equipment. After irradiation by microwave for 2 ~ 4 min (as indicated by TLC), the mixture was cooled to room temperature, dichloromethane was added, the mixture filtered and the filtrate washed with water and dried with anhydrous magnesium sulfate. The solvent was evaporated to give crude product, which was further purified by recrystallization or distillation.

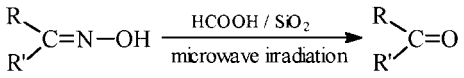

Table 1. Regeneration of Ketones from Oximes Using HCO_2H/SiO_2 in Dry Media Under Microwave Irradiation

Entry	Products[a]	Reaction Time (min)	M.P. (°C) or b.p. (°C) (Lit.)[15]	Yield (%)[b]
1		2	130/133.33 Pa (130/133.33 Pa)	86
2		2	155/133.33 Pa (155/133.33 Pa)	87
3	$C_6H_5COCH_3$	3	66–67/0.88 Pa (67/0.88 Pa)	92
4	$C_6H_5COC_2H_5$	4	82–84/1.4 Pa (84–85/1.4 Pa)	90
5	$4\text{-}O_2NC_6H_4COCH_3$	2	79.5–80.5 (80–81)	94
6	$3\text{-}O_2NC_6H_4COCH_3$	2	80–81 (81)	94
7	$4\text{-}ClC_6H_4COCH_3$	3	98–99/1.23 Pa (99/1.23 Pa)	93
8	$3\text{-}BrC_6H_4COCH_3$	3	115–117/1.23 Pa (117/1.23 Pa)	92
9	$4\text{-}HOC_6H_4COCH_3$	3	107–108 (109)	91
10	$4\text{-}CH_3C_6H_4COCH_3$	4	111–112/1.93 Pa (112.5/1.93 Pa)	91
11	$3,4\text{-}(CH_3)_2C_6H_3COCH_3$	4	88/0.45 Pa (88–90/0.53 Pa)	89
12	$C_6H_5COC_6H_5$	3	48–49 (48.5–49)	93
13		3	54–55 (56)	88
14	$C_6H_5COCOC_6H_5$	2	94–95 (95)	94

[a]All products were characterized by m.p. (or b.p.), IR spectra.
[b]Yields of the isolated products.

Based on these results, $HCOOH/SiO_2$ can be used as an excellent deoximation reagent for regeneration of ketones from oximes in dry media under microwave irradiation.

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