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Zeofen as a Catalyst for Cleavage of Semicarbazones and Phenyl Hydrazones Under Conventional Heating and Microwave Irradiation

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Semicarbazones and phenylhydrazones are oxidatively cleaved under conventional heating and microwave irradiation in solventless system to generate the corresponding carbonyl compounds by zeofen as catalyst.

Key Words: Semicarbazone, Phenylhydrazone, Zeofen, Microwave irradiation .

INTRODUCTION

Protection and deprotection of a functional group is almost inevitable in multistage organic synthesis[1]. Carbonyl compound derivatives such as phenylhydrazones and semicarbazones are important masked compounds of carbonyl groups[2]. Semicarbazones and phenylhydrazones are highly crystalline and are used for the characterization and purification of carbonyl compounds[3]. Regeneration of carbonyl compound from prepared semicarbazones and phenylhydrazones has received a significant attention in recent years[4] within the framework of Green chemistry[5], a noticeable improvement provided by the association of solvent free techniques and microwave activation[6]. The combination of solvent free reaction conditions and microwave irradiation leads to large reduction in reaction times, enhancements conversions and sometimes in selectivity with several advantages of the eco-friendly approached termed green chemistry. In preceding papers we introduced zeofen as a catalyst for the selective oxidation of alcohols under classical heating and microwave irradiation under solvent free conditions[7], oxidative cleavage of THP ethers in non-aqueous conditions[8], oxidative deprotection of TMS ethers under microwave irradiation in solventless system[9] and as an eco-friendly catalyst for deoximation[10]. In this communication we wish to report that zeofen is an excellent and efficient reagent for the oxidative cleavage of semicarbazones 1a-8a and phenylhydrazones 1b-8b to the corresponding compounds 2a-8a under classical heating and microwave irradiation.

EXPERIMENTAL

All products were known and their spectral and physical data were compared with those of authentic sample, Zeofen was prepared according to reported method[7].

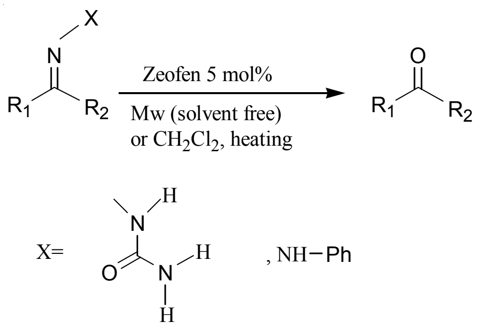
Typical procedure for oxidative cleavage of semicarbazones and phenyl hydrazones: Method A: A solution of substrate a or b (1 mmol) in dry CH_2Cl_2

(10 mL) was treated with catalytic amount of zeofen (0.05 mmol) and the reaction mixture was magnetically stirred at room temperature. The reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the solid residue was washed with CH_2Cl_2. Evaporation of solvent gave the corresponding carbonyl compounds.

Method B: Substrate a or b and zeofen (0.05 mmol) were crushed together so as to form an intimate mixture. This mixture was placed under microwave irradiation for appropriate time (Tables 1and 2). The corresponding aldehyde or ketone was extracted from the solid with CH_2Cl_2.

RESULTS AND DISCUSSION

The oxidative cleavage of semicarbazone of benzaldehyde 1a and phenylhydrazone of benzaldehyde 1b as model compounds occurred easily in CH_2Cl_2 at room temperature within 20 min to afford corresponding aldehyde (**Scheme-I**). To assess the generality of method, various semicarbazones and phenylhydrazones were oxidatively cleaved at room temperature at high yields and reasonable time (Tables 1 and 2).



Scheme-I

Although there has been increasing interest in reactions that proceed under microwave irradiation and solventless system[11], oxidation reactions are less often considered as candidates for microwave irradiation due to their unsafe and uncontrolable experimental conditions[12]. In connection with our interest in using microwaves to increase the rates of reactions, we have investigated the oxidative cleavage of semicarbazones and phenylhydrazones using zeofen under microwave irradiation. The regeneration of carbonyl compounds were carried out simply by using catalytic amount of zeofen (4.8-10 mol %) with 1 mmol of either phenylhydrazones or semicarbazones in a beaker under microwave irradiation (900 W) for 0.5-2.0 min. This solventless system procedure efficiently converts various semicarbazones and phenylhydrazones to their parent carbonyl compounds in excellent yields and short reaction time (Tables 1and 2).

When iron(III) nitrate was used without zeolite even in stiochiometric amount in these reactions, the conversion of semicarbazones and phenylhydrazones was only 50 % under conditions.

TABLE-1
OXIDATIVE CLEAVAGE OF PHENYLHYDRAZONES USING CATALYTIC AMOUNT OF ZEOFEN IN CH_2Cl_2 (METHOD A) AND UNDER MW IRRADIATION IN SOLVENTLESS SYSTEM (METHOD B)

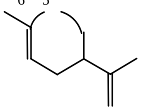
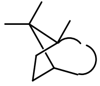
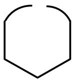
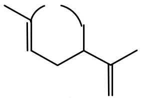
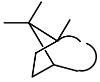
Substrate (phenyl-hydrazone)	R_1	R_2	Method	Time (min)	Product	Yield (%)
1a	H	C_6H_5	A	20.0	Benzaldehyde	89
			B	1.0		91
2a	H	o-$MeOC_6H_5$	A	20.0	2-Methoxybenzaldehyde	88
			B	0.5		92
3a	H	p-MeC_6H_5	A	20.0	4-Methylbenzaldehyde	87
			B	0.5		97
4a	H	o-$NO_2C_6H_5$	A	20.0	2-Nitrobenzaldehyde	77
			B	0.5		99
5a	H	p-$NO_2C_6H_5$	A	30.0	4-Nitrobenzaldehyde	58
			B	0.5		60
6a	H	o-OHC_6H_5	A	20.0	Salicylaldehyde	70
			B	1.0		99
7a	H	$CH=CHC_6H_5$	A	20.0	Cinnamaldehyde	60
			B	0.5		62
8a	C_6H_5	C_6H_5	A	20.0	Benzophenone	85
			B	2.0		92
9a			A	120.0	Carvone	–
			B	1.0		7
10a			A	120.0	Camphor	70
			B	1.0		87

TABLE-2
OXIDATIVE CLEAVAGE OF SEMICARBAZONES USING CATALYTIC AMOUNT OF ZEOFEN IN CH_2Cl_2 (METHOD A) AND UNDER MW IRRADIATION IN SOLVENTLESS SYSTEM (METHOD B)

Substrate (semi-carbazone)	R_1	R_2	Method	Time (min)	Product	Yield (%)
1b	H	C_6H_5	A	20.0	Benzaldehyde	70
			B	0.5		85
2b	H	o-$MeOC_6H_5$	A		2-Methoxybenzaldehyde	95
			B	0.5		99
3b	H	p-MeC_6H_5	A		4-Methylbenzaldehyde	87
			B	0.5		99
4b	H	p-$NO_2C_6H_5$	A		4-Nitrobenzaldehyde	–
			B	0.5		99
5b	H	o-OHC_6H_5	A		Salicylaldehyde	76
			B	0.5		99
6b	H	$CH=CHC_6H_5$	A		Cinnamaldehyde	65
			B	0.5		70
7b	C_6H_5	C_6H_5	A	20.0	Benzophenone	93
			B	0.5		99
8b	CH_3	C_6H_5	A	20.0	Acetophenone	80
			B	1.0		94

9b		A	20.0	Cyclohexanone	78
		B	1.0		86
10b		A	30.0	Carvone	40
		B	0.5		83
11b		A	30.0	Camphor	82
		B	0.5		99

Otherwise similar to these described above. Zeolite clearly aided the reproducibility and high activity of iron(III) nitrate. The mechanism and role of zeolite for this catalysis are not clear in this stage. It is also noteworthy to mention, that in the absence of zeolite molten ferric nitrate and or its degradation product(s) adhered to the walls of the reaction vessel, forming an intractable solid mass which made the isolation of carbonyl compound cumbersome and led to erratic results. It is noteworthy to mention that this procedure is effective for the selective cleavage of semicarbazones and phenylhydrazones of complex molecule such as camphor and carvone and interestingly, semicarbazone and phenylhydrazone of cinnamaldehyde underwent oxidative cleavage in high yields. During this oxidative cleavage C=C remaind intact.

In conclusion zeofen can be easily prepared from inexpensive and non-toxic materials serves as efficient reagent for oxidative cleavage of semicarbazones and phenylhydrazones under classical conditions at room temperature with high yields and under microwave irradiation in solvent less system in better yields and shorter reaction period.

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