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Solid State Cleavage of Semicarbazones with Cerium Ammonium Nitrate Supported by Wet Alumina

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Summary. Cerium ammonium nitrate on wet alumina rapidly regenerates carbonyl compounds from their corresponding semicarbazone derivatives under solvent-free conditions; the process is expedited by microwave irradiation.

Keywords. Semicarbazones; Alumina; Cerium ammonium nitrate; Microwave irradiation; Solvent-free system.

Introduction

Semicarbazones are useful protecting groups and are extensively used for isolation and purification of carbonyl compounds [1, 2]. Extensive studies on the deprotection of these derivatives have been carried out using various catalysts such as copper(II) chloride [3a], cation exchange resin [3b], clayfen [3c], potassium bromate [3d], zirconium sulfophenyl phosphonate, chlorotrimethylsilane/sodium nitrate or nitrite [3e], and ammonium persulfate/clay [3f]. These methods require high temperatures [3a–b], long reaction times, or involve toxic metal ions [3e, g, h] as catalysts. Consequently, there is a demand for the development of protocols using readily available and safer reagents under environmentally friendly conditions.

Different salts of Ce(IV) have been employed as versatile reagents in organic synthesis [4a–c]. In addition, Cerium(IV) as ceric ammonium nitrate has been used for the regeneration of carbonyl compounds from oximes and semicarbazones in nitric acid in a corrosive environment [5].

Reagents impregnated on mineral solid supports have gained popularity in organic synthesis because of their selectivity and ease of manipulation [6, 7]. During the course of our investigations on organic manipulations in solvent-free systems [8], we have observed a relatively useful microwave (MW) effect [8a–c]. The salient features of this MW approach are improved reaction rates and cleaner

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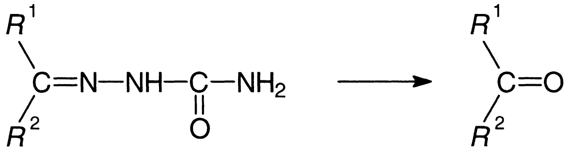

Scheme 1

reactions [9]. Microwave-assisted reactions under dry conditions [6, 7, 10] are especially appealing as they provide an opportunity to work with open vessels, thus avoiding the risk of high pressure, and with a possibility of upscaling the reaction on the preparative scale. In continuation of our ongoing efforts [8a–d] we envisoned the applicability of supported cerium ammonium nitrate to fulfil a variety of oxidative needs under solvent-free reaction conditions using microwaves. Here, we report a facile and rapid desemicarbazonation protocol using cerium ammonium nitrate (*CAN*) doped wet alumina.

Results and Discussion

Among the various solid supports examined, such as montmorillonite K-10, silica gel, and wet alumina, the latter proved to be superior. In the absence of wet alumina the reaction was sluggish, and a mixture was obtained.

Wet alumina was prepared by shaking neutral aluminum oxide with distilled water. The reagent was prepared by mixing cerium ammonium nitrate and a weight equivalent of wet alumina using a pestle and mortar. The reaction was conducted by mixing this reagent with neat semicarbazones.

In most cases, the reactions are completed upon simple mixing. However, gentle warming by microwaves accelerates some others (Table 1). The reactions are relatively clean; no tar formation was observed. Interestingly, no overoxidation occured.

Table 1. Cleavage of semicarbazones with *CAN* supported by wet alumina in a solventless system

R^1	R^2	Reaction time (s)	Yield[b] (%)
C_6H_5	H	10	90
C_6H_5	CH_3	20	86
C_6H_5	C_6H_5	40[a]	82
p-Cl–$C_6C_6H_4$	H	60[a]	85
o-Cl–C_6H_4	H	40[a]	88
m-Cl–C_6H_4	H	40[a]	82
o-NO_2–C_6H_4	H	40[a]	75
p-OH–C_6H_4	H	300[a]	85
Cyclohexyl		20[a]	88
CH_3	C_2H_5	20	85
$CH_3CH{=}CH$	H	20	68

[a] Reactions completed under microwave irradiation; [b] isolated yield

The reaction seems to be quite general. The semicarbazones of not only aromatic aldehydes and ketones, but also aliphatic aldehydes and cyclic ketones reacted smoothly to give the corresponding aldehydes and ketones. However, the reaction of crotonaldehyde semicarbazone gave a moderate yield of 60%, indicating a possibility of carbon–carbon double bond cleavage as detected by GLC.

In conclusion, an environmentally benign and safe oxidant on a solid support is introduced. Rapid reaction, high yield, and the use of inexpensive and non-corosive alumina instead of corrosive nitric acid under solvent-free conditions are attractive features of this protocol.

Experimental

All compounds are known and were identified by comparison with authentic samples (physical and spectroscopic data). Semicarbazones were prepared by reaction of aldehydes and ketones with semicarbazide hydrochloride and identified by their melting points and IR spectra.

Preparation of CAN/wet alumina

Aluminum oxide (1 g, Aldrich; Brockmann, ~150 mesh) was shaken with 2 cm^3 distilled H_2O. To this mixture, 1.09 g cerium ammonium nitrate (2 mmol) was added and crushed together in a mortar to form an intimate mixture.

Regeneration of semicarbazones

An appropriate semicarbazone (2 mmol) was thoroughly mixed with the above catalyst (2.09 g, equivalent to 2 mmol of *CAN*) using a spatula. An exothermic reaction ensues with darkening of the reagent and is completed almost immediately as confirmed by TLC (hexane:AcOEt = 8:2). The product is extracted into CH_2Cl_2 ($2 \times 25\,cm^3$) and passed through a small bed of silica gel to afford the pure carbonyl compound. In some cases, brief microwave irradiation (in an unmodified household microwave oven) completes the reaction (Table 1).

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