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Solid State Cleavage of Semicarbazones with Montmorillonite K-10 Supported *Bis*(trimethylsilyl)chromate under Microwave Irradiation

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Summary. Semicarbazones of aldehydes and ketones adsorbed on clay can be cleaved oxidatively to the corresponding carbonyl compounds under solvent-free conditions in high yields employing *bis*(trimethylsilyl)chromate and microwave irradiation.

Keywords. Semicarbazones; Carbonyl compounds; Microwave irradiation; Solvent-free conditions.

Mikrowellenunterstützte Spaltung von Semicarbazonen mit an Montmorillonit K-10 adsorbiertem *Bis*(trimethylsilyl)chromat im Festkörper

Zusammenfassung. An Ton adsorbierte Semicarbazone von Aldehyden und Ketonen können mit *Bis*(trimethylsilyl)chromat unter Bestrahlung mit Mikrowellen in einer Festphasenreaktion in hohen Ausbeuten oxidativ zu den ensprechenden Carbonylverbindungen gespalten werden.

Introduction

Semicarbazones are used not only to isolate and purify but also to protect carbonyl compounds during syntheses [1, 2]. Several procedures for regenerating carbonyl compounds from semicarbazones have been reported [1–19].

Microwave irradiation in organic synthesis is presently widely used. Its application in the case of inorganic solid supported reactions has been recently reviewed [20]. Solvent-free organic reactions or dry media techniques under microwave irradiation are one of the main topics of research in our laboratory [21, 22].

We have recently introduced montmorillonite K-10 supported *bis*(trimethylsilyl)chromate (*BTSC*) as an efficient reagent for oxidation of alcohols [23] and oxidative deprotection of trimethylsilyl [24] and tetrahydropyranyl [25] ethers. In this communication we demonstrate that montmorillonite K-10 supported *BTSC*

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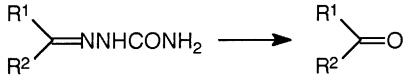
can efficiently and rapidly regenerate aldehydes and ketones from their semicarbazones using microwaves under solvent-free conditions.

Results and Disscusion

When *BTSC* [23] was mixed with benzaldehyde semicarbazone and irradiated with microwaves, after 5 min conversion to benzaldehyde was observed; however, a considerable amount of starting material was still present. In recent years, organic reactions with solid supported reagents [26] and the application of microwaves [27], especially under solvent-free conditions [28], have attracted attention because of enhanced selectivity, milder reaction conditions, and ease of manipulation. Among the various supports examined, such as alumina, silica, and montmorillonite K-10, the latter was found to be the most efficient. Benzaldehyde semicarbazone was mixed thoroughly with montmorillonite K-10 supported *bis*(trimethylsilyl)chromate and irradiated with microwaves to afford the parent aldehyde almost immediately and quantitatively. This reaction is rather general; semicarbazones of aromatic aldehydes and ketones as well as of aliphatic and unsaturated aldehydes reacted smoothly to give the corresponding aldehydes and ketones (Table 1). Unlike to other oxidative hydrolytic methods, the major drawback of overoxidation was not encountered. It should be mentioned that the semicarbazone of crotonaldehyde gave only a moderate yield of aldehyde showing that the reagent may cleave the carbon-carbon double bond.

In conclusion, montmorillonite K-10 supported *BTSC* mediated solvent-free microwave thermolycic is a convenient, selective, and environmentally benign desemicarbazonation protocol when compared to conventional solution phase or

Table 1. Cleavage of semicarbazones with montmorillonite K-10 supported *BTSC* under microwave irradiation and solvent-free conditions



R^1	R^2	Reaction time (sec)	Yiled (%)
C_6H_5	H	60	96
C_6H_5	CH_3	60	82
C_6H_5	C_6H_5	60	80
4-Cl-C_6H_4	H	120	90
2-Cl-C_6H_4	H	120	92
3-Cl-C_6H_4	H	60	80
2-NO_2-C_6H_4	H	180	82
4-OH-C_6H_4	H	60	82
Cyclohexyl		120	85
CH_3	C_2H_5	120	80
CH_3CH=CH	H	120	62

heterogeneous reactions. In addition, by development of a continuous microwave reactior for organic syntheses [29–30] this method may gain industrial application where the absence of solvents and the low costs of the method may lead to environmental and financial advantages.

Experimental

All compounds empolyed are known and were identified by comparison of their physical data with those of authentic samples. *Bis*(trimethylsilyl)chromate supported on montmorillonite K-10 was prepard according to Refs. [23–24].

General procedure

Montmorillonite K-10 supported *BTSC* (0.75 g, equivalent to 1.2 mmol of chromium(VI)) was mixed thoroughly with 1 mmol of semicarbazone and irradiated by microwaves (900 W) for the indicated time (Table 1). The progress of the reaction was monitored by TLC. After completion of the reaction, the solid phase was taken up in CH_2Cl_2, filtered, and washed with an excess of CH_2Cl_2. The filtrate was evaporated to dryness and purified by column chromatography using hexane:ethylacetate = 8:2 as eluent to afford the corresponding carbonyl compound (Table 1).

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