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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry Publication details, including instructions for authors and subscription information:

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Mukulesh Baruah^a, Dipak Prajapati^a & Jagir S. Sandhu^a

^a Division of Organic Chemistry (Drugs), Regional Research Laboratory, Jorhat, 785 006, Assam, India

Version of record first published: 11 Mar 2009.

To cite this article: Mukulesh Baruah , Dipak Prajapati & Jagir S. Sandhu (1998): Regeneration of Carbonyl Compounds from Semicarbazones Under Microwave Irradiations, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 28:22, 4157-4163

To link to this article: http://dx.doi.org/10.1080/00397919809458695

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REGENERATION OF CARBONYL COMPOUNDS FROM SEMICARBAZONES UNDER MICROWAVE IRRADIATIONS

Mukulesh Baruah, Dipak Prajapati and Jagir S. Sandhu*

Division of Organic Chemistry (Drugs) Regional Research Laboratory, Jorhat 785 006, Assam, India

Abstract: Semicarbazones 1 undergo facile cleavage to the corresponding carbonyl compounds 2 by bismuth trichloride under microwave irradiations in high yields.

There has been considerable interest in the development of mild techniques for the conversion of semicarbazones into their corresponding carbonyl compounds. This is because such derivatives of carbonyl compounds serve as efficient protecting groups for aldehydes and ketones in organic synthesis¹. Although literature enumerates quite a number of methods for the regeneration of carbonyl compounds from oximes² and hydrazones³, not many methods are available to regenerate carbonyl compounds from semicarbazones under mild conditions⁴. Methods so far developed to regenerate carbonyl compounds from semicarbazones, consist of hydrolytic (acid catalysed)¹ or oxidative or⁵ catalytic⁶.

^{*} To whom correspondence should be addressed.

and therefore are not satisfactory when sensitive groups are present elsewhere in the molecule. In view of the current thrust on catalytic processes, there is merit in developing truly catalytic cleavage of semicarbazones using inexpensive and nonpolluting reagents, Herein we wish to report the use of bismuth trichloride as a new catalyst for the cleavage of semicarbazones under microwave irradiation⁷. The reaction proceeds efficiently in high yields at ambient pressure within a few minutes time.



In a typical case, benzophenone semicarbazone (10 mmol), bismuth trichloride⁸ (2 mmol) and water (1 mL) were mixed together in tetrahydrofuran (10 mL) in an Erlenmeyer flask and placed in a commercial microwave oven (operating at 2450 MHz frequency and the power output is 490 Watt) and irradiated for 8 minutes. After completion (monitored vide TLC), the reaction mixture was allowed to reach room temperature and the corresponding benzophenone mp 49-51°C (Lit¹⁰ mp 49-51 °C) was obtained in 90% yield (entry 1) and there was no evidence for the formation of any side products. Similar treatment of other semicarbazones gave the corresponding carbonyl compounds 2 in 70 - 90% yields as summerised in the table. The same reaction was not equally effective when reacted thermally in wet tetrahydrofuran without microwave energy. The cleavage of semicarbazone was only 45% after 12 hours of refluxing. All the compounds obtained were characterised by infrared and ¹H NMR spectroscopy and finally by comparison with authentic samples.

Entry	Product ^b					
	-					
1	Benzophenone					
2	Acetophenone					
3	Cyclohexanone					
4	2-Cyclohexen-1-one					
5	3-Methyl-2-cyclohexen-1-one.					
6	4-Methylacetophenone					
7	4-Methoxyacetophenone					
8	4-Chloroacetophenone					
9	4-Nitroacetophenone					
10	Camphor					
11	Anisaldehyde					
12	Benzaldehyde					
13	3-Formyl chromone					
14	Cinnamaldehyde ^b					

Table	Bismuth	trichloride	catalysed	cleavage	of	semicarbazones	1	under
microws	ve irradiat	ions						

Reaction

4

7

10

10

8

10

8

10

10

11

5

10

5

15

time (min.)

Yield^a

(%)

85

90

70

86

85

80

86

75

80

75

72

70

75

55

^aYields refer to pure isolated products, characterised by IR, ¹H NMR and MS. ^bFurther increasing the reaction time gave no significant improvement in yields.

Several examples illustrating this novel and rapid procedure for the conversion of semicarbazones to parent carbonyl compounds are illustrated in the table. As shown in entry 4 & 5, even α,β -unsaturated ketonic semicarbazones were hydrolyzed without rearrangement of α,β -double bond using this new

mp/bp

(°C)

49-51(48.5-49)10

201(202)10

155(155)10

165-167(168)10

198-99(200)10

220-23(223)10

36-38(37-39)11

230-232 (232)11

79-80(80-81)11

178-179(179)11

245-247(248)10

177-178(179)10

152-153(152)12

247-248(248)10

catalyst. Functional groups such as halogen or nitro group were also inert to this catalyst and no by-product was observed (entry 8 & 9). Not only ketone semicarbazones but also aldehyde semicarbazones were hydrolysed without any side reactions, although the yields were a little lower for aldehyde semicarbazones (entry 11 to 14). Cinnamaldehyde semicarbazones for example, produced a mixture of products in moderate yields. Further increasing the reaction time gave no significant improvement in yields but rather decomposition of product occurred. The rate of catalytic cleavage of benzophenone semicarbazone was fast, requiring 0.2 equivalent of the catalyst and needing only 4 mins to complete the reaction. It should be also noted that the sterically hindered camphor semicarbazone had been successfully converted to camphor in 75% yield.

In summary, the present procedure for the regeneration of carbonyl compounds has some advantages over the existing methods and will make a useful and important addition to the present methodologies. The main advantages of this new method are mild reaction conditions, reduced reaction times, minimisation of side products and excellent yields.

Experimental

Melting points were determined by using a Buchi melting point apparatus and are uncorrected. The IR spectra were obtained on a Perkin-Elmer 237B IR spectrophotometer in KBr discs. All reagents were of commercial quality from freshly opened containers and were purchased from Aldrich Chemical Company and used without further purification. Solvents were dried according to standard procedures. The starting semicarbazones 1 are prepared from the corresponding carbonyl compounds by the usual methods⁹ and were freshly recrystallised before use. The commercial microwave oven used is operated at 2450 MHz frequency and the power output is 490 Watt.

General Procedure for the Regeneration of Carbonyl Compounds from Semicarbazones under Microwave Irradiation:

Benzophenone semicarbazone (2.40g, 10 mmol), bismuth trichloride⁸ (0.64g, 2 mmol) and water (1 mL) are mixed together in tetrahydrofuran (10 mL) in an Erlenmeyer flask covered with a glass funnel and placed in a commercial microwave oven (operating at 2450 MHz frequency and the power output is 490 Watt) and irradiated for 8 minutes. Upon completion (monitored vide TLC), the reaction mixture was allowed to reach room temperature, treated with water, extracted with dichloromethane (2 x 20 mL) and dried over anhydrous sodium sulphate. Removal of solvent and the residue on purification by column chromatography on silica gel using benzene:hexane (1:1) as the eluent gave the corresponding benzophenone (entry 1) mp. 49-51°C (Lit¹⁰ mp 48.5-49°C) in 90% (1.64g) yield and there is no evidence for the formation of any other products. Similarly other semicarbazones 1 are reacted under microwave irradiation and the corresponding carbonyl compounds 2 (entry 2 to 14) are obtained in 55-90% yields. All the compounds produced are characterised by compering the mp/bp, IR and ¹H NMR data with those of authentic samples.

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(Received in the U.S.A. 15 May 1998)