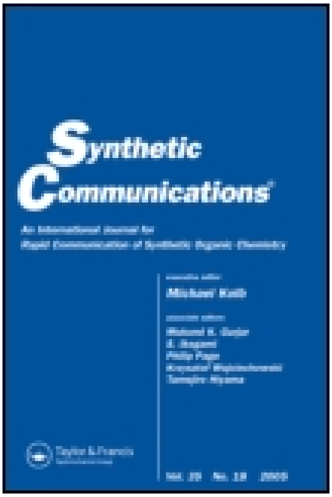

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Solid State Regeneration of Ketones From Semicarbazones Using Antimony Trichloride Under Microwave Irradiation

Alok Kumar Mitra [a], Aparna De [a] & Nilay Karchaudhur [a]

[a] Department of Chemistry, University of Calcutta, 92. Acharya Prafulla Chandra Road, Calcutta, 700 009, INDIA

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SOLID STATE REGENERATION OF KETONES FROM SEMICARBAZONES USING ANTIMONY TRICHLORIDE UNDER MICROWAVE IRRADIATION

Alok Kumar Mitra*, Aparna De and Nilay Karchaudhuri

Department of Chemistry, University of Calcutta
92, Acharya Prafulla Chandra Road, Calcutta – 700 009, INDIA

Abstract : Microwave irradiation of ketosemicarbazones with wet antimony trichloride under solvent-free condition provides a fast, efficient and simple method for the regeneration of ketones in good yields.

Protection of carbonyl compounds as semicarbazones is of great interest to organic chemists, as they are readily prepared and highly stable compounds[1]. Semicarbazones are extensively used for purification and characterization of carbonyl compounds[2]. Although a number of methods for the regeneration of carbonyl compounds from semicarbazones viz. sodium nitrite/glacial acetic acid[3], pyruvic acid[4], mercury (II) acetate, thallium (II) acetate, lead (IV) acetate[5], clayfen[6], nitrous acid[7], Dowex-50[8], tetrakis (pyridine) silver dichromate/benzene[9], copper chloride[10], 3-carboxypyridinium chlorochromate/CH_3CN[11], zirconium sulfophenyl phosphonate[12] have been reported, the discovery of newer efficient and fast methods is the goal of the organic chemists.

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* To whom correspondence should be addressed.

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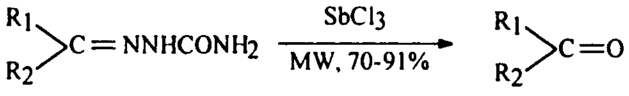
Recently, the wide applicability of microwave irradiation in chemical reaction enhancement[13] is due to high reaction rates with formation of cleaner products and the operational simplicity. The potentiality of microwave irradiation in MORE[14] chemistry is now a well established procedure.

In recent years the use of inorganic reagents[15] in solvent-free condition has rapidly increased, as these reaction often involve the milder condition, easier work up and higher selectivity than similar reactions using organic reagents in solution. Recently, an area of intense synthetic endeavor has been emphasized the use and design of reagents without any solvent to reduce the amount of toxic waste and byproducts arising from the chemical processes prompted by stringent environment protection law. Although antimony pentachloride[16] has been exploited extensively as useful reagent in various organic reactions, antimony trichloride[17] was not explored very much. In continuation of our ongoing programme to develop synthetic protocols utilising microwave irradiation under solvent-free conditions[18], we wish to report herein a solid state method for regeneration of ketones from semicarbazones using wet antimony trichloride under microwave irradiation (Scheme 1). The reaction proceeds efficiently in high yields at ambient pressure within a few seconds (Table 1). To the best of our knowledge this is the first report of the regeneration of ketones from semicarbazones using antimony trichloride. The optimum ratio of the substrate to



Scheme 1

Table-1 Microwave-assisted regeneration of ketones from semicarbazones using wet antimony trichloride

Entry	Semicarbazone	Product	Time (Sec)	Yield[a] (%)
1	Isobutyl methyl ketone semicarbazone	Isobutyl methyl ketone	9	70
2	Cyclohexanone semicarbazone	Cyclohexanone	12	70
3	Acetophenone semicarbazone	Acetophenone	10	90
4	4-Methylacetophenone semicarbazone	4-Methylacetophenone	6	87
5	4-Methoxyacetophenone semicarbazone	4-Methoxyacetophenone	9	89
6	4-Nitroacetophenone semicarbazone	4-Nitroacetophenone	11	80
7	6-Methoxytetralone semicarbazone	6-Methoxytetralone	15	88
8	2-Acetylnaphthalene semicarbazone	2-Acetylnaphthalene	12	91
9	Acetylacetone disemicarbazone	Acetylacetone	11	72
10	Benzil disemicarbazone	Benzil	8	81

[a]Yields refer to pure isolated products.

the reagent is found to be 1:1 (mole/mole). Reaction does not take place in dry condition also in the absence of the reagent. Stirring at room temperature for 3h also leads to regeneration of ketones.

The reagent has wide applicability for regeneration of ketones from aliphatic, aromatic ketosemicarbazones and disemicarbazones of α- and β-diketones.

Experimental

The IR spectra were run on Perkin-Elmer 782 spectrophotometer. ^1H NMR spectra were determined in d-chloroform solution on a FT NMR Bruker AM 300L operating at 300 MHz. The reactions were carried out in a domestic microwave oven (BPL-SANYO, BMO-700T, 1200W).

General Procedure

A mixture of semicarbazone (1 mmol) and antimony trichloride (1 mmol, E. Merck) moistened with water (0.5 ml) was taken in a 25 ml Erlenmeyer flask[10]. The flask was then placed in an alumina bath (heat sink) inside a microwave oven operating at medium power (600W) and irradiated for the specified time. After completion of the reaction (monitored by TLC) the product was extracted with dichloromethane (2x5 ml) and washed with brine and dried over anhydrous sodium sulphate. All the products were characterized by ^1H NMR spectroscopy and by comparison with infrared spectra of authentic samples.

In conclusion, we have developed a solvent-free method for the facile conversion of a variety of ketosemicarbazones to ketones in solid state using wet antimony trichloride under microwave irradiation.

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19. To arrest the low boiling products (entries 1,2 and 9), the reactions were carried out in a 100 ml Erlenmeyer flask fitted with a funnel as a loose top, upon which a round bottomed flask containing ice was placed to serve as a condenser.

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