

Note

Microwave assisted convenient and facile regeneration of carbonyl compounds from semicarbazones, phenylhydrazones and tosylhydrazones using phosphoric acid in solvent-free conditions

Krishna Banerjee, Alok Kumar Mitra &
Amarendra Patra*

Department of Chemistry, University of Calcutta, 92, A. P. C.
Road, Calcutta 700 009, India

E-mail: amarendra@satyam.net.in

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Microwave irradiation of semicarbazones, phenylhydrazones and tosylhydrazones of carbonyl compounds with phosphoric acid under solvent-free conditions provides a fast, efficient and simple method for regeneration of carbonyls in excellent yields.

Keywords: Microwave irradiation, semicarbazones, phenylhydrazones, tosylhydrazones, carbonyl compounds, phosphoric acid

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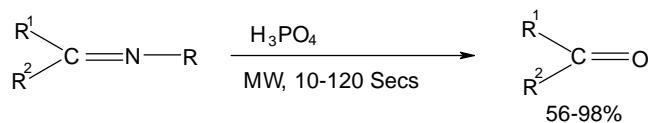
Developing mild and efficient methods for the cleavage of imine derivatives to afford carbonyl compounds continues to be a significant aspect of organic chemical transformation. Semicarbazones, phenylhydrazones and tosylhydrazones are highly stable and readily prepared compounds, which are used extensively for the protection of carbonyl groups¹ and for the purification and characterization of carbonyl compounds². Some of the methods of earlier reports for deprotection of ketone using conventional method as well as microwave irradiation involved, i) ammonium persulphate - Al_2O_3 (ref. 3a), bismuth trichloride^{3b}, sodium periodate - SiO_2 (ref. 3c), hypervalent iodine^{3d}, poly [4-vinyl-*N,N*-dichlorobenzenesulfonyl amide]⁴, manganese triacetate⁵, urea nitrate⁶ and low valent titanium⁷ from oximes, ii) MnO_2 ⁸, clay-ferric nitrate⁹, 3-carboxypyridinium chlorochromate¹⁰ and formic acid¹¹ from phenyl hydrazones, iii) copper (II) chloride dihydrate¹² from semicarbazones, iv) TBHP¹³ from oximes and tosylhydrazones. Some of these reagents suffer from one or the other disadvantages. Besides, some of the reagents, viz., thallium (III)¹⁴, lead (IV)¹⁵, chromium (VI)¹⁶ which regenerate

aldehydes are toxic. So the search for faster and solvent-free reaction conditions using new reagent is the goal of chemists.

In recent years the growing interest in the application of microwave irradiation¹⁷ in chemical reaction enhancement is due to high reaction rates and formation of cleaner products. The solvent-free^{18,19} reactions are specially appealing for providing an eco-friendly system. In continuation of our ongoing programme¹⁹ to develop synthetic protocols utilizing microwave irradiation under solvent-free conditions, herein we wish to report the regeneration of carbonyls in fair to excellent yields and in short times from semicarbazones, phenylhydrazones and tosylhydrazones of eleven aldehydes and nine ketones of varied nature exploiting phosphoric acid (**Scheme I**). Phosphoric acid is an environment friendly reagent because pure phosphoric acid is odourless and when diluted, it is not injurious to health. It is used for the manufacture of certain food stuffs such as gelatin and soft drinks²⁰. It is also used in the production of various salts in the fertilizers, detergents and dentifrice industries, the annual output of phosphoric acid being more than ten million metric tons only in USA²¹. However a little is known in the literature for the use of phosphoric acid in synthetic applications²² other than its use in dehydrations of 2° and 3° alcohols²³, cycloaromatization of carbinol acetals by H_3PO_4 (ref. 24) and very recently regeneration of amino acids from their *N*-BOC derivatives²⁵. The reactions were usually completed within 10 – 120 seconds at power level 5 (600 W) and resulted in 56-98 % yield (**Table I**).

Experimental Section

The IR spectra were run on a Perkin-Elmer FT IR-RXI spectrophotometer. The ¹H NMR spectra were



$R = -\text{NHCONH}_2, -\text{NHPh}, -\text{NHTs}$

$R^1 = \text{alkyl or aryl}$

$R^2 = \text{H, alkyl or aryl}$

Scheme I

Table I—Regeneration of carbonyl compounds from their semicarbazones, phenylhydrazones and tosylhydrazones

Substituents R ¹	R ²	From semicarbazone		From phenylhydrazone		From tosylhydrazone	
		Time (Sec) Required	Isolated Yield (%)	Time (Sec) Required	Isolated Yield (%)	Time (Sec) Required	Isolated Yield (%)
(CH ₃) ₂ CH	H	10	66	-	-	-	-
(CH ₃) ₂ CH CH ₂	H	10	69	12	74	15	70
Ph CH ₂	H	20	72	25	76	30	78
4(OMe)C ₆ H ₄	H	40	72	40	76	50	98
4(NO ₂)C ₆ H ₄	H	80	65	60	86	40	69
3,4(OMe) ₂ C ₆ H ₃	H	40	69	50	89	40	68
3,4(OCH ₂ O)C ₆ H ₃	H	20	80	40	82	10	70
3(OH)4(OMe)C ₆ H ₃	H	40	56	40	72	30	68
3(OCH ₂ C ₆ H ₅)C ₆ H ₄	H	25	74	40	69	-	-
4(OCH ₂ C ₆ H ₅)3(OH)C ₆ H ₃	H	30	69	40	79	10	94
3(OCH ₂ C ₆ H ₅)4(OH)C ₆ H ₃	H	20	92	30	78	15	71
(CH ₃) ₂ CH CH ₂	CH ₃	30	74	25	72	50	79
-CH ₂ CH ₂ CH ₂ CH ₂ -		120	72	30	79	100	80
C ₆ H ₅	CH ₃	60	78	50	80	60	72
4(Me)C ₆ H ₄	CH ₃	60	75	60	79	60	76
4(OMe)C ₆ H ₄	CH ₃	40	84	40	82	50	82
4(NO ₂)C ₆ H ₄	CH ₃	120	84	35	84	60	89
2(OH)C ₆ H ₄	CH ₃	50	77	60	85	40	76
C ₆ H ₅	C ₆ H ₅	70	76	40	71	60	74
-6 (OMe)-(o) C ₆ H ₃ -CH ₂ CH ₂ CH ₂ -	-	80	74	50	72	-	-

recorded in CDCl₃ solution on a Bruker AM 300L NMR spectrometer operating at 300.13 MHz. The reactions were carried out in a microwave oven (BPL-SANYO, BMO-700T, 1200 W).

General procedure. A mixture of semicarbazones (0.5 mmole) or phenylhydrazones (0.5 mmole) or tosylhydrazones (0.5 mmole) and phosphoric acid (1 mL) were taken in a 50 mL Erlenmeyer flask, kept over an alumina-bath, irradiated for specified time (**Table I**) and the reaction was monitored by TLC. The product was extracted with ether (3 × 10 mL), washed with brine and dried over anhydrous sodium sulphate. Evaporation of the solvent afforded the products in excellent yield (**Table I**). All the products were characterized by ¹H NMR spectroscopy and from close similarity with IR spectra of authentic samples.

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