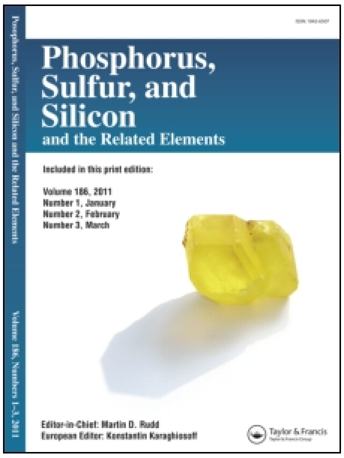

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Bis(Trimethylsilyl)Chromate: An Efficient Reagent for Cleavage of Phenylhydrazones

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Bis(Trimethylsilyl)Chromate: An Efficient Reagent for Cleavage of Phenylhydrazones

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Phenylhydrazones are converted to their parent carbonyl compounds by silica-gel supported bis(trimethylsilyl) chromate.

Keywords Bis(trimethylsilyl)chromate; carbonyl compound; phenylhydrazones; protection

Protection and deprotection of a functional group almost is inevitable in multistage organic synthesis.[1] Phenylhydrazones frequently are used to protect carbonyl compounds. They also serve as important synthetic intermediates and can be used preferably for isolation, purification, and characterization of aldehydes and ketones.[2] Because of these significances, a plethora of reagents and methods, such as ammonium persulfate–clay $Zr(t\text{-}ButO)_4$,[3] as a catalyst and tert-butylhydroperoxides as oxidant;[4] benzyl-triphenylphosphonium peroxodisulfate;[5] prolinium chlorochromate;[6] potassium ferrate under microwave irradiation in solvent free conditions,[7] hypervalent organoiodine,[8] and thallium acetate[9] have been reported. These methods have their own merits and drawbacks.

The application of bis(trimethylsilyl) chromate as catalyst in organic transformation has been developed in our laboratory.[10–17] In view of extending this research and in our interest in the cleavage of phenylhydrazones,[18] we now report a simple, efficient, and high-yielding method for the conversion of phenylhydrazones to their corresponding carbonyl compounds.

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The reagent Bis(trimethylsilyl)chromate (BTSC) was prepared by the treatment of hexamethyldisiloxane with CrO_3 in CH_2Cl_2.

Initially, we treated the phenylhydrazone of benzaldehyde with this reagent in refluxing CH_2Cl_2. The progress of reaction was monitored by TLC. The reaction was sluggish and more seriously molten; BTSC adhered to the walls of the vessel, making the work up cumbersome.

At this point, we contemplated to change the solvent and implement a homogeneous catalysis. However, homogeneous catalysts generally are connected with the problem of separation and wasted inorganics, which are too difficult to reuse. In addition, order to prepare conditions for homogeneous catalysis, we needed high boiling-point solvents. These problems could be minimized principally by a heterogeneously catalyzed reaction.

The use of supported reagent[19] has attracted interest because of improved selectivity, reactivity, and ease of manipulation.

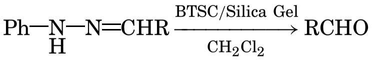
Application of solid support for a heterogeneous catalysis of an organic reaction has been one of our research interests.[20] To use BTSC for the cleavage of phenylhydrazones, we examined various mineral supports such as montmorillonite K-10, zeolites, alumina, and silica gel in different low boiling-point solvents. After some preliminary experimentation, it was found that BTSC that was supported on silica gel in a mixture of chloroform and water as solvents provided the best results in terms of the formation of pure products for the cleavage of phenylhydrazones. In the absence of silica gel, the reaction is very slow, the yield is very low, and the isolation of products from the ensuing residues is difficult. Surprisingly, when CH_2Cl_2 or $CHCl_3$ were used as a solvent, the yield was lower than when using a mixture of chloroform and water. The procedure involves the simple mixing of BTSC with silica gel and refluxing this mixture with a phenylhydrazone in a mixture of 1:1 $CHCl_3$ and H_2O. To establish the generality of the method, various phenylhydrazones were cleaved by the aforementioned procedure. No over oxidation to carboxylic acid was observed.

In summary, the presented methodology offers an attractive, efficient, and high-yielding method for the cleavage of phenylhydrazones to the corresponding carbonyl compounds, using a silicon reagent.

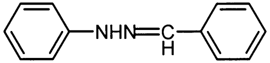
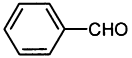
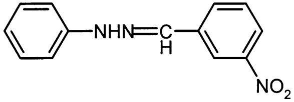
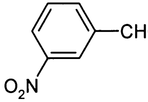
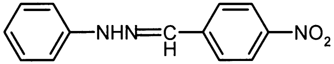
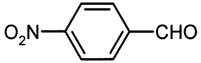
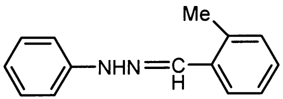
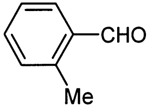
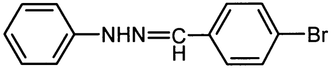
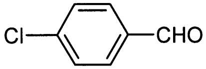
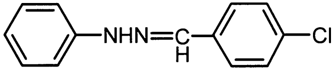
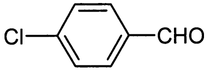
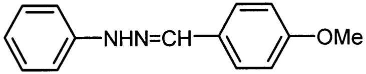
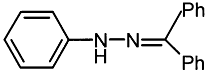
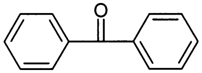
EXPERIMENTAL

Phenylhydrazones were prepared according to the literature.[2] All products were known and their physical data was compared with those of authentic samples. Yields refer to GC analysis, an Agilent 6890 Series GC System.

TABLE I Regeneration of Phenylhydrazones Using Silica-Gel Supported BTSC Under Non-Aqueous Conditions



$$Ph\!-\!\underset{H}{N}\!-\!N\!=\!CHR \xrightarrow[CH_2Cl_2]{BTSC/Silica\ Gel} RCHO$$

Entry	Substrate	Time (min)	Product	Yield (%)	mp (°C) or bp (°C)/760 Torr Found	Report
1		9		98	176–177	178.1
2		25		97	57–58	58
3		25		97	106–108	106
4		18		97	200	200
5		9		97	66	67
6		10		98	212	213–214
7		9		96	250	249.5
8		5		98	304–306	305.5

[a] Yields refer to GC-MS analysis.

PREPARATION OF BIS(TRIMETHYLSILYL)CHROMATE[10–18] SUPPORTED ON SILICA GEL

To a solution of hexamethyldisiloxane (6.4 mL, 0.03 mol) in dry CH_2Cl_2 (20 mL), CrO_3, (3 g, 0.03 Mol) was added. The reaction mixture was stirred in a 50°C bath. Solid CrO_3 dissolved and the dark red mixture became homogeneous. Silica gel (13 g) per-dried at 120°C overnight was added to the warm reaction mixture and the resulting mixture was stirred for a further 5 h. The solvent and other volatile components were removed under reduced pressure to afford 19 g of the supported BTSC oxidant.

REGENERATION OF CARBONYL COMPOUNDS FROM PHENYLHYDRAZONES

General Procedure

Silica-gel supported BTSC (0.93 g, equivalent to 1.5 mmol) was refluxed with a phenylhydrazone (1 mmol) in a mixture of $CHCl_3$ and H_2O (10 mL) for the indicated time. Progress of the reaction was monitored by TLC. Upon the completion of the reaction, the reaction mixture was filtered. The organic layer was separated and evaporated to dryness to afford the corresponding carbonyl compound (Table I).

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