Facile oxidative cleavage of semicarbazones, tosylhydrazones and phenylhydrazones with Oxone®

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An efficient and mild methodology for the oxidative cleavage of semicarbazones, tosylhydrazones and phenylhydrazones using Oxone® is described.

Developing mild and efficient methods for the selective cleavage of nitrogen-containing derivatives to afford carbonyl compounds continues to be a significant aspect of organic chemical transformation. Semicarbazones, tosylhydrazones and phenylhydrazones serve as important synthetic intermediates and are also extensively used for the purification and characterization of aldehydes and ketones. As a result, a number of methods have been described in literature for the regeneration of carbonyl compounds from such nitrogen derivatives, but most of them suffer from several limitations such as expensive and hazardous reagents, higher temperatures, longer reaction periods and tedious procedures. Consequently, there is a need for the development of protocols using readily available and safer reagents which lead to high recoveries of carbonyl compounds.

Among the known oxidising agents potassium peroxymonosulfate (2KHSO₅, KHSO₄, K₂SO₄), commercially sold as Oxone®, is a convenient, inexpensive and powerful oxidant used for the transformation of a wide range of functional groups. In this connection, we have recently reported a mild oxidation of nitriles to amides. Herein, we wish to report an exceptionally simple and efficient method for regenerating carbonyl compounds quantitatively from their corresponding semicarbazones, tosylhydrazones and phenylhydrazones using Oxone®.

As illustrated in Table I, oxidative cleavage of nitrogen-containing derivatives to the corresponding carbonyl compounds was performed with potassium peroxymonosulfate in glacial acetic acid. In contrast, treatment of the title derivatives of α,β-unsaturated carbonyl compounds does not result in satisfactory regeneration of the parent carbonyl compounds, but leads to a mixture of products.

In conclusion, the use of Oxone® permits the conversion of semicarbazones, tosylhydrazones and phenylhydrazones into the corresponding aldehydes and ketones, in a new and convenient way. This procedure can be easily scaled up, and the reagent used

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All carbonyl derivatives were prepared by known literature procedures.

Products were characterized by comparison of their melting points, IR and 1H NMR spectra with authentic samples.

Yields refer to isolated pure product.

Note

Table I — Oxidative cleavage of semicarbazones, tosylhydrazones and phenylhydrazones with Oxone.

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being cheap and non-toxic, it could well prove to be the oxidising reagent of choice.

**Experimental Section**

**General procedure.** A mixture of carbonyl derivative (aldehyde or ketone) (2.5 mmoles), glacial acetic acid (5 mL), potassium peroxymonosulphate (5.0 mmoles) and water (10 mL) was stirred at 40 - 45 °C for the specified reaction period (cf. Table I). The reaction was monitored by TLC. After completion of the reaction, the product was extracted with ether (2 x 25 mL), washed with saturated brine, aq. 10% NaHCO₃, dried (anhyd. Na₂SO₄) and the solvent removed in vacuo to afford the product in excellent yields (83-94%).

**References**


