3-Benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (BMTC), a new reagent for regeneration of carbonyl compounds from their N,N-dimethyl hydrazones

B Balram, B Ram* & P K Sai Prakash
Department of Chemistry, Osmania University, Hyderabad 500 007, India.

Received 7 June 1999; accepted 30 August 1999

N,N-Dimethyl hydrazones undergo oxidative cleavage to corresponding carbonyls by employing BMTC, in good to excellent yields at room temperature.

N,N-Dimethyl hydrazones are of increasing importance as protecting groups in carbonyl chemistry, especially in controlled C-C bond formation reactions18. A variety of methods have been reported for the regeneration of carbonyl compounds from N,N-dimethyl hydrazones, such as oxidative cleavage with nitronium and nitrosonium salt9, cupric ion catalyzed hydrolysis10, singlet oxygen11, sodium perborate12, magnesium monoperoxyphthalate13, baker's yeast14 and others15 are employed. Recently dimethyl sulphate and potassium carbonate has been reported for regeneration of carbonyl compounds16.

3-Benzyl-5-(2-hydroxyethyl)-4-methyl-1, 3-thiazolium chloride (BMTC) was prepared by quaternization of 5-(2-hydroxyethyl)-4-methylthiazole with benzyl chloride in acetonitrile17, which is hygroscopic in nature. The BMTC in the presence of bases, act as catalyst for the preparation of acyloins and benzoins18 from aldehydes and for addition of aldehydes to electrophilic double bonds19.

In this paper we wish to describe the use of BMTC as a mild oxidising agent, for the cleavage of N,N-dimethyl hydrazones to carbonyl compounds. The reaction of N,N-dimethylhydrazones with BMTC is fast at room temperature and completes in 1 hr, giving the corresponding carbonyl compounds in good yields. The results are described in Table I.

Cleavage of N,N-dimethyl hydrazone by BMTC.

General procedure. To a vigorously stirred solution of N,N-dimethylhydrazones (10 mmoles) in chloroform (20 mL) was added BMTC (2.69 g, 10 mmoles), and the mixture stirred for 1 hr at room temperature. The completion of the reaction was monitored by TLC, at regular intervals. The reaction mixture was washed with water and then extracted with chloroform. The organic layer was dried over Na2SO4, filtered and evaporated in vacuo, to afford the crude product, which was purified by column chromatography on silica gel (60-120 mesh) using ethyl acetate-hexane (1:1) system as eluant.

The products were characterized as their 2,4-dinitrophenyl hydrazones, and by comparison of their spectral properties with those of the authentic sample and also by HPLC analysis.

In summary, this new method for the regeneration of carbonyl compound has some practical merits over...
Table 1 — Deprotection of N,N-dimethyl hydrazones of substrate 1 by BMTC leading to the formation of original ketone 1.

<table>
<thead>
<tr>
<th>N,N-dimethyl hydrazones of substrate 1</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>94</td>
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<tr>
<td>2</td>
<td>92</td>
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<td>3</td>
<td>93</td>
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<td>8</td>
<td>90</td>
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<td>9</td>
<td>92</td>
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applicability for the regeneration of aldehydes and ketones with sensitive functional groups from their N,N-dimethylhydrazones derivatives. The present method of deprotection of N,N-dimethylhydrazones using BMTC is thus an efficient mild oxidizing agent and very inexpensive method.

References

8 For asymmetric C-C bond formations via chiral hydrazones see:
17 a) Stetter H & Khulmann H, Angew Chem Int Edn, 13, 1974, 539.
   b) Stetter H & Khulmann H, Tetrahedron, 1974, 4505.

previously reported methods, such as easy preparation of reagents, mild reaction conditions and has broad