Pergamon

SCIENCE DIRECT®

Tetrahedron Letters 44 (2003) 9055–9056

TETRAHEDRON LETTERS

$SiBr_4$/wet silica gel as an efficient heterogeneous system for cleavage of C=N

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Received 27 August 2003; revised 24 September 2003; accepted 25 September 2003

Abstract—A new and efficient method for the cleavage of oximes, hydrazones and semicarbazones has been achieved with $SiBr_4$/wet silica gel.

Oximes, hydrazones and semicarbazones are useful protecting[1] groups and are extensively used for purification and characterization of carbonyl compounds. Their synthesis from non-carbonyl compounds[2] provides an alternative pathway to aldehydes and ketones. There has been considerable interest in the development of mild techniques for the conversion of oximes into their corresponding carbonyl compounds.[3–5] Although some of the known methods are carried out under mild reaction conditions, most of them require drastic conditions, high temperature, long reaction times, expensive, toxic or not readily available reagents, they need to be freshly prepared and tedious work-up procedure. Recently, some microwave irradiation techniques have been developed[6,7] which are valuable from the synthetic standpoint but extreme precaution have to be taken as these reactions were perfomed under microwave irradiation or ultrasonic irradiation with an oxidant. Most of the known methods deal for the regeneration of carbonyl compounds from oximes only, a little attention has been paid for the regeneration of carbonyl compounds from hydrazones and semicarbazones.[8–10]

Table 1. Deprotection of oximes, hydrazones and semicarbazones with $SiBr_4$/wet silica gel at room temperature

Entry	Substrate	Time (min)	Product	Yield[a] (%)
1	4-Chloroacetophenone semicarbazone	10	4-Chloroacetophenone	93
2	Benzophenone semicarbazones	18	Benzophenone	91
3	Acetophenone semicarbazone	24	Acetophenone	86
4	4-Methoxyacetophenone semicarbazone	14	4-Methoxyacetophenone	89
5	Benzaldehyde semicarbazone	17	Benzaldehyde	83
6	3-Nitrobenzaldehyde semicarbazone	22	3-Nitrobenzaldehyde	87
7	4-Bromobenzaldehyde semicarbazone	15	4-Bromobenzaldehyde	89
8	Cyclohexanone semicarbazone	14	Cyclohexanone	90
9	4-Methoxybenzaldehyde semicarbazone	18	4-Methoxybenzaldehyde	88
10	Benzophenone phenylhydrazone	26	Benzophenone	87
11	4-Chloroacetophenone phenylhydrazone	15	4-Chloroacetophenone	91
12	4-Bromobenzaldehyde phenylhydrazone	19	4-Bromobenzaldehyde	90
13	2-Nitrobenzaldehyde phenylhydrazone	28	2-Nitrobenzaldehyde	79
14	Cyclohexanone oxime	16	Cyclohexanone	85
15	Acetophenone oxime	220	Acetophenone	83[b]
16	Benzophenone oxime	280	Benzophenone	89[b]
17	Benzaldehyde oxime	68	Benzaldehyde	90
18	4-Bromobenzaldehyde oxime	35	4-Bromobenzaldehyde	87

[a] Yields refer to pure isolated products, characterized by IR, ^1H NMR and MS.

[b] Under reflux condition.

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doi:10.1016/j.tetlet.2003.09.208

In this paper I wish to report a convenient and efficient method for the regeneration of carbonyl compounds from semicarbazones, hydrazones and oximes using $SiBr_4$ in the presence of wet silica gel.

Table 1 summarizes the results of the conversions of various oximes, hydrazones and semicarbazones to their corresponding carbonyl compounds. Semicarbazones and hydazones were deprotected very rapidly at room temperature into their corresponding carbonyl compounds. It should be noted that above mentioned reactions did not proceed using wet silica gel alone, $SiBr_4$ alone, $SiBr_4$ with ordinary silica gel alone even after prolonged heating. The products of the reaction with $SiBr_4$ in the presence of wet silica gel were isolated very simply by filtering the mixture and evaporating the solvent from the filtrate. The method has advantages in terms of yield, heterogeneous nature, cheapness and availability of reagents, short reaction times and easy work-up and will make a useful and important addition to the present methodologies.

The oximes, hydrazones and semicarbazones were prepared by standard procedures.[11] In a typical procedure for deprotection of semicarbazones, 4-chloroacetophenone semicarbazone (5.27 g, 25 mmol), $SiBr_4$ (4.7 mL, 37 mmol), silica gel (12 g), water (12 mL) in carbon tetrachloride (125 mL) was stirred at room temperature for 10 min. The reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the solid residue was washed with carbon tetrachloride. The filtrate was washed with sodium bicarbonate solution (100 mL), water (100 mL), dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel, (eluted hexane–ethyl acetate: 8/2) to afford 4-chloroacetophenone in 93% yield and there was no evidence for the formation of any side products. Similar treatment of oximes and hydrazones gave the corresponding carbonyl compounds in 79–91% yield as summarized in the Table 1.

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