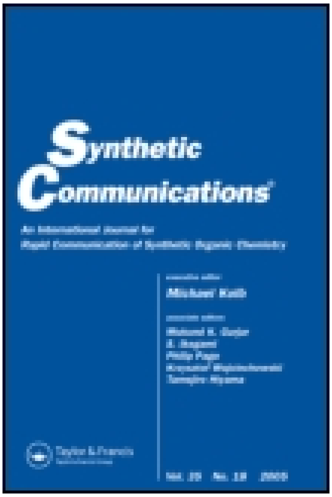

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tert-Butyl Hypoiodite for Deoximation

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tert-Butyl Hypoiodite for Deoximation

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Abstract: *tert*-Butyl hypochlorite and *tert*-butyl hypobromide react with aldoximes and convert them into hydroximinoyl chloride and bromide, respectively; however, under the same reaction conditions, *tert*-butyl hypoiodite deoximates aldoximes and ketoximes to give corresponding aldehydes and ketones in high yield ($>94\%$) in a short reaction time (~ 20 min).

Keywords: Deoximination, oximes, *tert*-butyl hypoiodite

INTRODUCTION

There is a continued interest in the development of procedures for the effective generation of carbonyl compounds from the corresponding oximes, especially under mild conditions. There are several oxidative methods available for regeneration of carbonyl compounds from their corresponding oximes. These methods include use of Bismuth nitrate pentahydrate,[1] peroxomonosulfuric acid supported on silica gel,[2] *tert*-butyl hydroperoxide,[3] iodine in acetonitrile,[4] ammonium persulfate ion,[5] chromium trioxide–silica gel–microwave irradiation,[6] sodium periodate,[7] nickel diperiodate,[8] periodic acid,[9] and hypervalent iodine compounds.[10] In spite of the many reagents available, there is still scope for newer reagents. Here we report use of *tert*-butyl hypoiodite in carbon tetrachloride for the oxidative regeneration of carbonyl compounds from their oximes. Previously it was reported that *tert*-butyl hypochlorite and *tert*-butyl hypobromite in carbon tetrachloride

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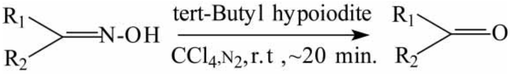
react with oxime to produce hydroximinoyl chloride and bromide respectively, with no reported deoximation.[11]

tert-Butyl hypoiodite was prepared by the reaction of *tert*-butyl hypochlorite with iodine in dry carbon tetrachloride in situ. Oximes were synthesized as per the literature report.[12] The deoximation was carried out by addition of stock solution of the reagent to a stirred solution of the oximes in carbon tetrachloride. More than 94% pure carbonyl compounds were recovered from the organic layer after the usual workup. Examples illustrating conversion of oximes to parent carbonyl compounds are listed in Table 1. The rate of deoximation was neither affected by electron-withdrawing or electron-donating substituents at the *para*-position. Even the sterically hindered camphor oxime could be successfully converted into camphor in high yield. It was observed that benzaldehyde methoxime (entry 15) did not undergo deoximation.

GENERAL PROCEDURE

The reagent *tert*-butyl hypoiodite (0.48 g of *tert*-butyl hypochlorite and 1.12 g of iodine in 20 mL of dry carbon tetrachloride) were added to a stirred solution

Table 1. Transformation of oximes to the corresponding carbonyl compounds using *tert*-butyl hypoiodite[a]



Entry	Carbonyl compound[b]	Time (min)	Yield (%)[c]
1	Benzaldehyde	15	96
2	4-Nitrobenzaldehyde	20	94
3	4-Methoxybenzaldehyde	20	96
4	4-Chlorobenzaldehyde	15	93
5	4-Methyl benzaldehyde	15	96
6	Cyclohexanone	15	96
7	Acetophenone	15	94
8	4-Methoxyacetophenone	20	96
9	4-Chloroacetophenone	20	95
10	4-Fluroacetophenone	20	96
11	4-Methylacetophenone	15	96
12	Benzil	15	95
13	Camphor	15	94
14	Octanal	20	96
15	Benzyldehyde O-methyloxime	No reaction	—

[a] All reactions were carried out at rt in dry CCl_4 under N_2 atmosphere.
[b] Structures confirmed by IR, ^1H NMR, and mp/bp.
[c] Yields are of the isolated products.

of 4-methylbenzaldoxime (0.5 g, 3.70 mmol) in carbon tetrachloride (20 mL) dropwise at room temperature under a stream of nitrogen. The stirring was continued until the oxime disappeared (TLC). The reaction mixture was diluted with addition of methylene dichloride and water. The organic layer was separated, washed with 5% cold sodium thiosulphate solution and water (50 mL), dried over sodium sulphate, and concentrated to give almost pure 4-methyl benzaldehyde (0.426 g, 96%).

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