



ELSEVIER

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com



Preliminary communication/Communication

[Hydroxy(tosyloxy)iodo]benzene-mediated regeneration of carbonyl compounds by cleavage of carbon nitrogen double bonds

Deepak K. Aneja^{a,*}, Pooja Ranjan^a, Loveena Arora^a, Om Prakash^{a,*},^c^a Department of Chemistry, Kurukshetra University, Kurukshetra, Haryana 136119, India^b Department of Chemistry, G. D. C. Memorial College, Bahal, Bhiwani, Haryana 127028, India^c Manav Bharti University, Solan, Himachal Pradesh 173229, India

ARTICLE INFO

Article history:

Received 10 July 2013

Accepted after revision 28 October 2013

Available online 4 July 2014

Keywords:

Hypervalent iodine(III) reagents

[Hydroxy(tosyloxy)iodo]benzene (HTIB)

Iodobenzene diacetate (IBD)

Hydrazones

Oxidative cleavage

Regeneration of carbonyl compounds

ABSTRACT

[Hydroxy(tosyloxy)iodo]benzene (HTIB)-mediated regeneration of carbonyl compounds from various derivatives of carbonyl compounds of aryl and heteroaryl hydrazines containing adjacent nitrogen atoms is reported. These types of hydrazones cleaved oxidatively, giving back carbonyl compounds with HTIB, while cyclisation occurred with iodobenzene diacetate (IBD).

© 2014 Published by Elsevier Masson SAS on behalf of Académie des sciences.

[Hydroxy(tosyloxy)iodo]benzene (HTIB, PhI(OH)OTs) is a versatile hypervalent iodine(III) reagent that has numerous applications in organic synthesis [1]. Important applications of HTIB are: α -functionalization of ketones [2] ring expansion [3] ring contraction [4] ring tosyloxylation [5] α -iodination [6] preparation of iodonium salt [7] synthesis of α,β -tosyloxyketones and their conversion into pyrazoles [8] isoxazoles [9] and synthesis of various other organic compounds [10].

The regeneration of the carbonyl functionality is an important step in organic synthesis. The recovery of parent ketones and aldehydes has classically involved acid

hydrolysis [11]. However, non-acidic methods are of special significance while dealing with compounds containing acid-sensitive groups [12]. So, considerable interest has been aroused in the development of mild and non-acidic methods for the cleavage of hydrazones, oximes, semicarbazones, thiosemicarbazones, etc. In this regard, a review of protection and deprotection of functional groups in organic synthesis by heterogeneous catalysis has been published by Sartori et al. [13] Though several methods have been employed for the regeneration of the carbonyl functionality, there is scope for the development of a newer and simpler methodology. The common deprotection protocols involve the use of hazardous heavy metal salts, for example mercury(II) chloride [14] and of toxic reagents such as SeO₂, (PhSeO)₂O, which besides being costly reagents also add to waste-disposal problems [15]. Similarly, reagents such as lead tetraacetate [16] thallium(III) nitrate [17] manganese dioxide [18] Y [19] and ZSM-5 [20] chlorochromate [21] ammonium chlorochromate adsorbed on alumina [22] iodic

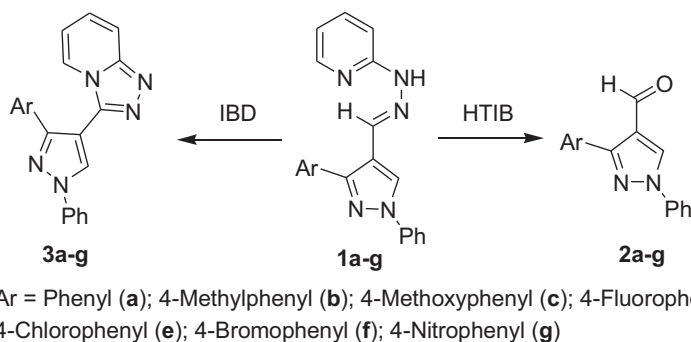
* Corresponding authors.

E-mail addresses: dk_aneja@rediffmail.com (D.K. Aneja),

ranjanpooja011@gmail.com (P. Ranjan),

loveena.arora22@gmail.com (L. Arora),

dromprakash50@rediffmail.com (O. Prakash).



Scheme 1.

acid [23] *N*-bromo-*N*-benzoyl-4-toluenesulfonamide [24] vanadyl acetylacetonate [25] aqueous phosphoric acid [26] and clayfen [25] have also been utilized for the regeneration of carbonyl compounds. However, some of these methods have suffered from different drawbacks such as requirements for refluxing temperature, tedious work-up, drastic conditions, long reaction times, undesired chemical yields, and use of toxic reagents. Recently, microwave irradiation has also been developed, which is valuable from the synthetic standpoint. But extreme precautions have to be taken as these reactions are performed under microwave irradiation or ultrasonic irradiation with an oxidant [27].

Moriarty et al. [28] developed an hypervalent iodine(III)-mediated methodology for the regeneration of various carbonyl compounds from oximes using iodobenzene diacetate (IBD). Further, Barton et al. [29] proposed a method involving the iodine(III)-mediated oxidation of various hydrazone derivatives of keto esters using HTIB, IBD, and [bis(trifluoroacetoxy)iodo]benzene (BTIB), which has been reported for the regeneration of parent carbonyl compounds. Parent ketones were also regenerated from semicarbazones using IBD [30].

In connection with our ongoing programme directed towards the use of hypervalent iodine(III) compounds as unique reagents in organic synthesis, we have recently reported the simple and efficient iodine(III)-mediated cleavage of carbonyl derivatives of dehydroacetic acid (DHA) with HTIB and IBD [31]. Various derivatives of carbonyls, such as aryl/heteroaryl hydrazones, oximes, semicarbazones and thiosemicarbazones, gave the parent carbonyl back after reaction with either HTIB or IBD. Both reagents showed a similar behaviour in the cleavage of derivatives of carbonyl compounds. Encouraged by these

observations, we further extended our research to study the behaviour of these two reagents towards carbonyl derivatives of other heterocyclic moieties and obtained some interesting results.

First, we carried out the oxidation of pyridylhydrazones of 4-formylpyrazoles (**1a–g**) with HTIB in dichloromethane (DCM) and we observed that oxidative cleavage¹ occurred smoothly in this case, giving back the parent carbonyl compounds (**2a–g**)². However, in our previous investiga-

¹ Initially the reaction of hydrazone was attempted with 1.1 equiv of HTIB in dichloromethane at room temperature. The following observations were made: (a) HTIB started dissolving; (b) the colour of the reaction medium changed from yellow to reddish brown; (c) a characteristic smell of iodobenzene was observed after evaporating the solvent from the reaction mixture. All these changes indicated the occurrence of the reaction, which was supported by the monitoring the TLC of the reaction mixture. The reaction was completed in 4 h. The product obtained was found to be the parent 4-formyl pyrazole (by comparison of TLC, melting point and NMR and IR data with authentic sample) in 50% yield. To optimize the results of oxidative cleavage, the reaction of hydrazone was attempted by increasing the molar ratio of the reagent, i.e. with 2.2 equiv of HTIB in DCM at room temperature. The colour of the reaction mixture changed immediately from yellow to brown black. Usual work-up of the reaction afforded the starting carbonyl compound in 80% yield. Thus, it was found that increasing the molar ratio of HTIB not only increases the yield, but also improves the neatness of the reaction. Encouraged by these successful results, we studied the scope of the HTIB mediated oxidative cleavage with other derivatives. The effect of the solvent was also tested by using different solvents, i.e. methanol, ethanol, and acetonitrile. The reaction proceeded with equal efficacy in acetonitrile, but with poor yield in ethanol and methanol. Therefore, acetonitrile and DCM are found to be suitable solvents for the oxidative cleavage of carbonyl derivatives of various aromatic aldehydes. As expected, this procedure involving HTIB was also successful for effective cleavage of semicarbazones and thiosemicarbazones derived from simple ketones such as cyclohexanone and acetophenone etc.

² General experimental conditions: HTIB was prepared from IBD and *p*-toluenesulfonic acid monohydrate in acetonitrile. IBD and all other chemicals used were purchased from commercial sources and were used without further purification. ¹H NMR was recorded on a Bruker 300 MHz instrument using tetramethyl silane (TMS) as an internal standard. IR spectra were recorded with a PerkinElmer 1800 FT-IR spectrophotometer. General cleavage procedure: To a stirred suspension of hydrazone (0.000589 mol) in DCM (15 mL) was added HTIB (0.00129 mol) in portion in 10 min at room temperature in open air atmosphere. The colour of the reaction mixture changed from red/yellow to brown. The progress of the reaction mixture was monitored by TLC. Stirring was continued for 10–60 min. After completion of the reaction, the solvent was distilled off and the resulting residue was triturated with petroleum ether (boiling range 60–80 °C) to remove the iodobenzene. The product obtained was purified by recrystallization and column chromatography using petroleum ether and ethyl acetate as eluents in 60–80% yield.

Table 1
Oxidative cleavage of carbonyl derivatives (**1a–g**) with HTIB.

Sr. no.	Reactant	Reference	Product	Time (in min)	Melting point (°C)	Yield (%)
1	1a	35	2a	30	140	80
2	1b	35	2b	30	122	82
3	1c	35	2c	30	121	83
4	1d	35	2d	30	148	78
5	1e	35	2e	30	110	77
6	1f	35	2f	30	132	82
7	1g	35	2g	30	165	85

Download English Version:

<https://daneshyari.com/en/article/170379>

Download Persian Version:

<https://daneshyari.com/article/170379>

[Daneshyari.com](https://daneshyari.com)