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Novel use of BiOCl as an efficient and selective reagent for cleavage of 2,4-dinitrophenylhydrazones to carbonyl compounds

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Abstract: A novel use of bismuth oxychloride (BiOCl) as an efficient and selective catalyst for the clean cleavage of 2,4-dinitrophenylhydrazones under mild conditions is reported. The reactions proceed very smoothly, and the yields are good to excellent. Over oxidation of aldehydes to carboxylic acid and the formation of by-products were not observed. The catalyst could be recovered and reused for at least four reaction cycles without considerable loss of reactivity.

Keywords: bismuth oxychloride; aldehydes; hydrazones; ketones; selective.

INTRODUCTION

Hydrazones are well-known and synthetically useful derivatives of aldehydes and ketones. They are usually formed easily from carbonyl compounds and hydrazines in a reversible reaction.[1] Hydrazones are important derivatives in carbonyl chemistry and are used extensively as protecting, activating, and directing groups.[2]

Regeneration of carbonyl compounds from stable and readily prepared oximes, hydrazones and semicabazones has received considerable attention in recent years.[3–6] There are only a few reports available dealing with these reactions.[7–11] Although some are realized under mild conditions, most of these regenerations are often hazardous or use very toxic, expensive, or not readily available reagents, or reagents which need to be freshly prepared.[12–14] Thus, there is still a need to develop new and facile procedures for the regeneration of carbonyl compounds from 2,4-dinitrophenylhydrazones.

In continuation of a systematic study and research on oxidation methods,[15–19] herein, a new simple and selective method for the conversion of 2,4-dinitrophenylhydrazones to their corresponding aldehydes and ketones by the novel use of bismuth oxychloride is reported.

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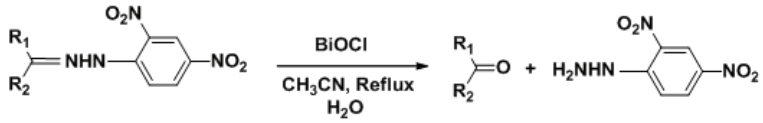
According to a literature search, there is not a great deal of work on the use of BiOCl as an oxidant and hence, this is the first report on the use of BiOCl as a reagent for the regeneration of the carbonyl group from 2,4-dinitrophenylhydrazones that act as a catalyst.

The simple reaction of different hydrazones by BiOCl in acetonitrile under reflux conditions gave the corresponding carbonyl compounds in good yields (Scheme 1).



Scheme 1. Cleavage of hydrazones by BiOCl.

EXPERIMENTAL

Chemicals and apparatus

Chemicals were purchased from Merck, Fluka and Aldrich chemical companies. The solvents were used as received. All products were known and identified by comparison of their m.p., b.p., IR and NMR data with those reported for the authentic samples. All yields refer to the isolated products. The progress of the reaction was monitored by TLC. The IR and ^{1}H-NMR spectra were recorded on a Shimadzu infrared spectrophotometer FT-IR, model IR Prestige 21 (KBr pellets), and a 90 MHz Jeol FT-NMR spectrometer, respectively. The ^{1}H--NMR chemical shifts were measured relative to TMS.

BiOCl was prepared according to previously reported procedure.[20] The 2,4-dinitrophenylhydrazones were prepared by a standard procedure.[21]

General procedure for the cleavage of hydrazones by bismuth oxychloride:

A solution of the hydrazone (1 mmol) in acetonitrile (10 mL) was refluxed for 10 min. Then BiOCl (1 mmol) was added to the solution and the mixture was refluxed for the appropriate time, as indicated in Table I. After completion of the reaction (TLC monitored), the reaction mixture was cooled to room temperature and H_2O (1 mmol) was added and the mixture stirred for 10 min. Then the solvent was evaporated and $CHCl_3$ or THF was added. After stirring the mixture for 10 min, the solid residue was filtered off and washed with $CHCl_3$ or THF (10 mL). Evaporation of the solvent gave the pure carbonyl products in excellent yields.

The products were characterized by their physical constants and IR and NMR spectra, which were compared with those of authentic samples.[22-31]

Recovery of the BiOCl

The residue on the filter paper was separated, HCl was added, the pH of the aqueous solution adjusted to 3 and the mixture stirred until the BiOCl was dissolved. The mixture was filtered (2,4-dinitrophenylhydrazine was separated as residue on the filter paper), Na_2CO_3 (5 % aqueous solution) was added to the filtrate and the pH of the aqueous solution was adjusted to 8–9.

After stirring at room temperature for 30 min, the resulting precipitate was filtrated and washed with deionized water several times. Finally, the white powders of BiOCl were obtained by drying the precipitate at 80 °C for 5 h.

RESULT AND DISCUSSION

The results illustrated in Table I indicate that the reaction was successful for a variety of aliphatic and aromatic 2,4-dinitrophenylhydrazones (Scheme 1).

TABLE I. Conversion of 2,4-dinitrophenylhydrazones to the corresponding carbonyl compounds by BiOCl; reaction conditions: hydrazine, 1 mmol, BiOCl, 1 mmol, H_2O, 1 mmol, CH_3CN; under reflux

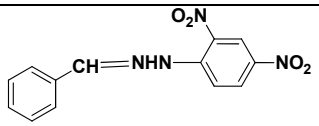
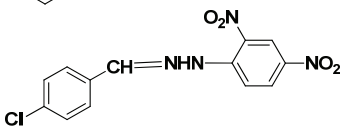
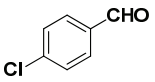
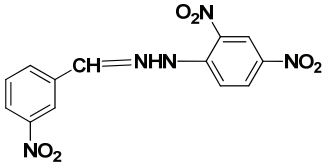
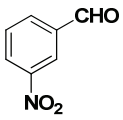
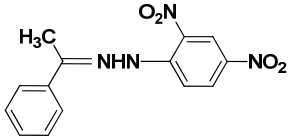
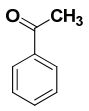
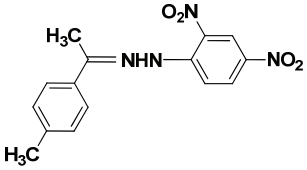
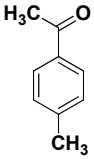
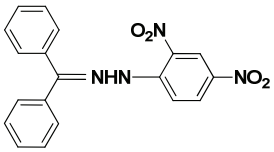
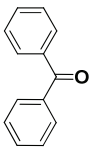
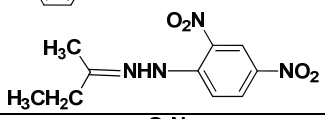
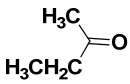
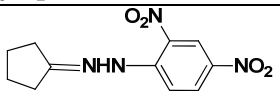
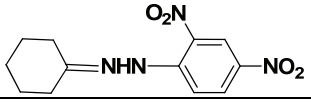
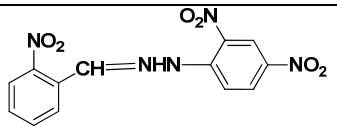
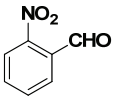
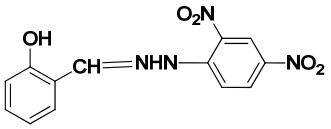
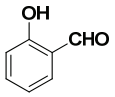
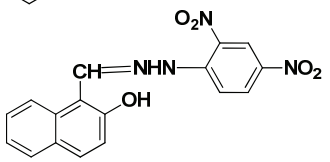
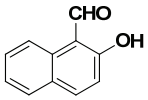
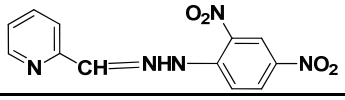
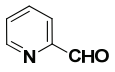
No.	Reactant	Product	Time, h	Yield[a], %
1			2:20	85[22]
2			2:15	82[22]
3			2	78[22]
4			3:15	92[22]
5			2:10	89[23]
6			1	90[22]
7			2:35	92[24,25]
8			1:15	81[26]
9			1:20	88[27]

TABLE I. Continued

No.	Reactant	Product	Time, h	Yield[a], %
10			3:20	70[28]
11			4	85[29]
12			4:25	85[30,31]
13			2:50	60[27]

[a]Isolated yields

All these carbonyl derivatives were converted back to their corresponding aldehydes and ketones in acetonitrile as the optimal solvent among the tested solvents, including: methanol, ethanol, chloroform, diethyl ether and acetonitrile, taking benzophenone 2,4-dinitrophenylhydrazone as a representative example (Table II).

TABLE II. Optimization of the solvent

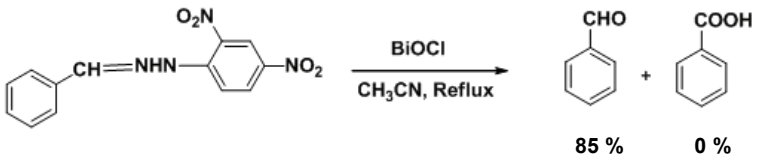
Entry	Solvent	Time, h	*T* / °C	Yield, %
1	MeOH	1	64	65
2	EtOH	1	78	70
3	$CHCl_3$	1	62	60
4	$(C_2H_5)_2O$	1	40	10
5	CH_3CN	1	80	90

Moreover, the reactions were run with different amounts of BiOCl. On analyzing the different results, it was concluded that the best reaction conditions were 1 mmol of oxidant BiOCl in CH_3CN media under reflux conditions.

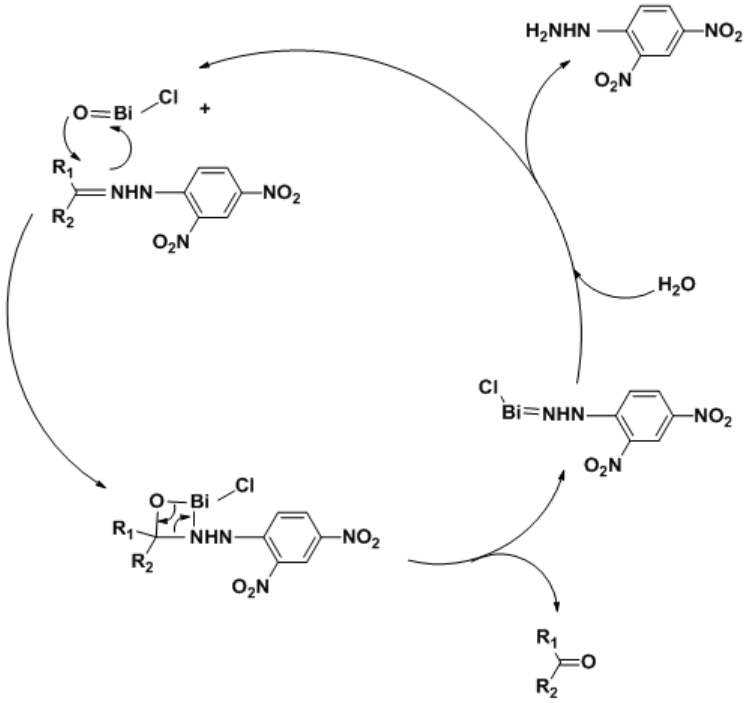
A sterically hindered ketone hydrazine was successfully cleaved to the corresponding ketone in good yield.

The hydrazones of aldehyde were converted into the corresponding aldehydes and no acid, due to oxidation of the regenerated aldehyde, was formed (entries 1–3 and 10–13, Scheme 2).

Based on the above results, a plausible reaction mechanism is shown in Scheme 3.



Scheme 2. Selective cleavage of hydrazone.



Scheme 3. Proposed mechanism for the cleavage of hydrazones.

Catalyst reuse and stability

An important advantage of BiOCl in these reactions is its facile recovery from the reaction mixture and reusability. The catalyst reuse and stability was checked using benzophenone 2,4-dinitrophenylhydrazone as a model substrate. The recovery of catalyst was very easy. The products are soluble in $CHCl_3$ or THF, while the catalyst remains insoluble. The catalyst was separated from the reaction mixture after each experiment by simple filtration.

As shown in Table III, the BiOCl catalyst was reusable four times and its activity did not show any significant decrease.

TABLE III. Reusability of BiOCl catalyst in the hydrolysis of benzophenone 2,4-dinitrophenylhydrazone

Run No.	Time, h	Yield[a], %
1	1	90
2	1:30	83
3	1:45	75
4	2	70

[a]Isolated yield

CONCLUSIONS

In this study, oxidation of the aldehydes to carboxylic acids and the formation of by products were not observed. Moreover, the synthesis of the catalyst (bismuth oxychloride) is very simple and the required starting materials are commercially available and cheap. The stability and activity of the catalyst are other advantages of this reagent. The catalyst could be recovered and reused for at least four reaction cycles without considerable loss of reactivity**.**

The striking features of the proposed method are availability, the cost of reagent, easy preparation of the catalyst, easy and clean work-up procedure (most do not require chromatography), absence of the formation of oxidation products due to the high selectivity and mild nature of the catalyst, high yields and recovery and reusability of the catalyst.

Overall, this simple, clean, selective and efficient procedure for the hydrolysis of various hydrazones to carbonyl compounds on a medium to large scale could be recommended.

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ИЗВОД

НОВА ПРИМЕНА BiOCl КАО ЕФИКАСНОГ И СЕЛЕКТИВНОГ РЕАГЕНСА ЗА РАСКИДАЊЕ 2,4-ДИНИТРОФЕНИЛХИДРАЗОНА ДО КАРБОНИЛНИХ ЈЕДИЊЕЊА

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Приказана је нова примена бизмут-оксихлорида као ефикасног и селективног реагенса за раскидање 2,4-динитрофенилхидразона под благим реакционим условима. Реакције се одигравају без потешкоћа у добром до одличном приносу. Није уочена оксидација алдехида до карбоксилних киселина или формирање других споредних производа. Реагенс се може изоловати из реакционе смеше, и поновно користити у бар четири наредна реакциона циклуса без значајнијег губитка реактивности.

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