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DABCO-Bromine Complex: A Novel Oxidizing Agent for Oxidative Deprotection of THP and Silyl Ethers and Semicarbazones to Corresponding Carbonyl Compounds

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Abstract: A tetrameric DABCO-bromine complex was synthesized, characterized, and utilized as a novel active bromine complex for the oxidative deprotection of THP and silyl ethers and semicarbazones to carbonyl compounds.

Keywords: DABCO-bromine complex, deprotection, oxidation, semicarbazones, silyl ethers, Tetrahydropyranyl ethers

INTRODUCTION

Silyl and THP (tetrahydropyranyl) ethers are extensively used as protective groups for alcohols in synthetic chemistry because of their low cost, efficiency

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of preparation, stability under the intended reaction conditions, and easy and selective removal.^[1] A variety of methods for the selective deprotection of these protective groups have been developed, but the direct synthesis of carbonyl compounds from THP or silyl ethers is not widespread in the literature.^[2]

Semicarbazones also serve as important synthetic intermediates, and they can be used for isolation, purification, and characterization of aldehydes and ketones.^[3]

Although there are many methods for deprotection of silyl and THP ethers and semicarbazones to the corresponding carbonyl compounds, many of these methods have severe limitations such as tedious workup, long reaction times, low yields, high temperatures, and also the use of organic solvents, Lewis acid catalysts, expensive reagents, etc. Thus, the introduction of new methods, inexpensive reagents, and environmentally friendly reaction conditions for such functional group transformations is still in demand. It is also interesting that the use of water as a solvent makes the reaction interesting from both an economical and environmental point of view. ^[4]

We have recently reported the oxidation of alcohols,^[5] deoximation,^[6] desemicarbonization,^[7] and oxidative deprotection of silyl^[8] and THP ethers^[9] using hexamethylenetetramine bromine and used DABCO as the catalyst for the synthesis of N-arylphthalimide^[10] and the desilylation of silyl ethers.^[11]

1,4-Diazabicyclo[2,2,2]octane (DABCO)–bromine complex is easily prepared from bromination of DABCO with liquid bromine at room temperature. It has been used as an oxidant for conversion of alcohols to their carbonyl compounds.^[12] In this letter, we describe another use of DABCO–bromine complex in the transformation of silyl and THP ethers and semicarbazones to their carbonyl compounds in water at 80 °C.

RESULTS AND DISCUSSION

DABCO-bromine complex is a yellowish solid that is stable in exposure to light, air, and water. Its structure was characterized by X-ray crystallogra-phy^[13] [Eq. (1)].

$$4\text{DABCO} + 14\text{Br}_2 \xrightarrow[\text{DABCO-bromine}]{} [(\text{H}_2\text{DABCO})_2(\text{HDABCO})_2(\text{Br})_2(\text{Br}_3)_4]$$
(1)

It is a homogeneous nonhygroscopic solid, which can be stored for months without losing its activity. It had no offensive of bromine or amine odor.

To find the optimum reaction conditions for oxidative deprotection of THP and silyl ethers, we carried out several reactions, changing the molar ratio of substrate to reagent, temperature, and solvents. Our results revealed that the highest yield is obtained with a 1:1/6 molar ratio of substrate to reagent in water at 80°C (Scheme 1).

DABCO-Bromine Complex



Scheme 1.

The results are shown in Table 1. As seem in Table 1, THP and silyl ether of 1-pentanol converted to the corresponding aldehyde in 90% and 95% yield respectively after 20 min. To show the generality of this procedure, we carried out the cleavage of a variety of THP ethers. As indicated in Table 1, aliphatic

Yield Time Entry Substrate Product^a (min) $(\%)^{b}$ 1 OTHP 20 90 СНО 2 сно 25 92 OTHP 3 СНО 25 90 OTHP сно 30 93 4 OTHP MeC MeO 5 30 89 OTHP OTHP 6 35 87 7 сно 35 88 OTHP Bŕ В́г

Table 1. Oxidative deprotection of tetrahydropyranyl and silyl ethers with DABCO-bromine complex in water

(continued)

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Entry	Substrate	Product ^a	Time (min)	Yield $(\%)^b$
8	OTHP		35	84
9	NO2 OTHP	NO ₂ CHO	30	74
10	OTHP	СНО	30	91
11	OSiMe ₃	СНО	20	95
12	OSiMe ₃	СНО	30	95
13	OSiMe ₃	СНО	30	90
14	OSiMe ₃	СНО	25	89
15	OSiMe ₃		35	86
16	OSiMe ₃	°	35	90
17	OSiMe ₃ Br	CHO	40	87

Table 1. Continued

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(continued)

Table 1. Continued

Entry	Substrate	Product ^a	Time (min)	Yield $(\%)^b$
18	OSiMe ₃		40	85
19	OSiMe ₃ NO ₂	NO ₂ CHO	55	77

^{*a*}All products were characterized spectroscopically (¹H NMR, IR) and showed physical and spectral data in accordance with their expected structure in comparison with authentic samples.

^bThe yields refer to isolated products.

THP ethers (Table 1, entries 1 and 5), aromatic THP ethers (Table 1, entries 2–4 and 6–9), and α,β -unsaturated THP ether (Table 1, entry 10) were efficiently cleaved to the corresponding carbonyl compounds in good yields. The yields were diminished when an NO₂ group was present on the aromatic ring (Table 1, entry 9) and longer reaction times had no impact on the yield. THP ethers containing a double bond (Table 1, entry 10) were also oxidized to the parent carbonyl compounds. It is worth mentioning that no bromination of the double bond took place. Similarly, secondary silyl ether (Table 1, entries 15, 16, and 18) were cleaved to the corresponding carbonyl compounds. The products were characterized by recording IR, ¹H NMR spectra, and elemental analyses and comparing them with authentic samples. No overoxidation products were detected in the case of aldehydes.

As indicated in Table 2, we regenerated some semicarbazones to their corresponding carbonyl compound with DABCO–bromine complex in water with good yields.

The positive features of the present method are summarized as follows: 1) ease of operation; 2) excellent yields, and 3) environmental consciousness: no organic solvent is used in the reaction, and only a small amount is needed in workup.

EXPERIMENTAL

Preparation of the Tetrameric DABCO-Bromine Complex

A solution of bromine (20.0 g, 125 mmol) in chloroform (100 mL) was added dropwise with stirring to a solution of DABCO (6.72 g, 60 mmol) in

Table 2. Regeneration of carbonyl compounds from semicarbazone with DABCO-bromine complex

Entry	Substrate	Product ^a	Time (min)	Yield $(\%)^b$
1	CH=NNHCONH ₂	СНО	20	90
2	CH=NNHCONH ₂ OMe	CHO	15	92
3	CI CH NNHCONH ₂	СНО	20	89
4	Me C==NNHCONII ₂	Br	20	95
5	Br Me C=NNHCONH ₂	Ph	25	87
6	$CH_3(CH_2)_3CH = NNHCONH_2$	CH ₃ (CH ₂) ₃ CHO	15	92

^{*a*}All products were characterized spectroscopically (¹H NMR, IR) and showed physical and spectral data in accordance with their expected structure in comparison with authentic samples.

^bThe yields refer to isolated products.

chloroform (100 mL). A yellow solid appeared as the bromine was taken up. The mixture was stirred for an additional 1 h, and then the yellow solid was collected by vacuum filtration. Yield 23.12 g (98%), decomp. $160-165^{\circ}$ C.

General Procedure

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To a suspension of DABCO–Br₂ (0.262 g, 0.166 mol) in water (15 mL) in a round-bottomed flask, an appropriate amount of the substrate (1 mmol) was added. The reaction mixture was stirred and warmed to 80° C until the yellow color of the complex disappeared. The progress of the reaction was

DABCO-Bromine Complex

monitored by thin-layer chromatography (TLC) using petroleum ether/ethyl acetate (8:2) as eluent. Upon completion of the reaction, ether was added to reaction mixture and was washed with solution of 1% HCl. The aqueous layer was separated, and the organic layer was washed with 3% sodium bicarbonate and water respectively. The organic solution was dried over MgSO₄, filtered, and evaporated to dryness under reduced pressure to afford the pure corresponding carbonyl compound.

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