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Synthesis, characterization and structure of a tetrameric DABCO-bromine complex: a novel oxidizing agent for oxidation of alcohols to 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 oxidation of alcohols to carbonyl compounds. © 2005 Published by Elsevier Ltd.

1. Introduction

Alcohol oxidation yielding aldehydes and ketones is a chemical transformation of primary industrial importance in the fine chemicals industry as carbonyl compounds are precursors of a variety of valuable fine chemicals including fragrances, vitamins and drugs.¹ Reagents of choice for oxidation of alcohols to carbonyl compounds are pyridinium chlorochromate (PCC),² Swern³ and Dess–Martin⁴ reagents, PCC catalyzed oxidation with periodic acid,⁵ silica gel supported InBr₃ and InCl₃,⁶ etc.⁷ We have recently reported the oxidation of alcohols,⁸ deoximation,⁹ desemicarbonization,¹⁰ and oxidative deprotection of silyl ethers¹¹ and THP ethers¹² using hexamethylenetetramine bromine and used DABCO as the catalyst for the synthesis of *N*-arylphthalimide¹³ and the desilylation of silyl ethers.¹⁴

In this letter, we describe the characterization and structure of a bromine complex of its use as a selective oxidant in organic chemistry. The reagent was prepared by the exothermic addition of molecular bromine to 1,4-diazabicyclo[2.2.2] octane (DABCO) in chloroform.

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A yellow solid appeared as bromine was taken up. The mixture was stirred for an additional 1 h and the yellow solid was filtered off and crystallized from acetonitrile to give single crystals appropriate for X-ray crystallography. The crystal structure of the DABCO–bromine complex has been already reported by others,¹⁵ but our data are better.

The oxidation reaction was conducted by refluxing the DABCO-bromine complex with an appropriate amount of an alcohol in a mixture of dichloromethane and water. The reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC (petroleum ether/ethyl acetate 8:2). To establish the generality of the method, various alcohols including allylic, benzylic, primary and secondary were oxidized with this reagent in 15 min-5 h to give the corresponding carbonyl compounds in excellent yields. The results are shown in Table 1. The oxidation of allyl alcohols was carried out under the mildest conditions, needing only 15 min to be completed. An allylic alcohol was oxidized regioselectively in the presence of other hydroxyl groups. No product of over-oxidation to carboxylic acids was observed. Concerns about the safety of adding molecular bromine to amines may be voiced, however, the addition of bromine to DABCO was observed to have only a moderate exotherm. The DABCO-bromine complex was a homogeneous non-hygroscopic solid, which was stable at room temperature and not affected

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Entry	Substrate	Reaction time (h)	Product	Yield (%)
1	СН2ОН	4	СНО	97
2	СІ—СН2ОН	5	СІ—СНО	98
3	MeO CH ₂ OH	4	МеО-СНО	97
4	O2N CH2OH	5	O ₂ N CHO	87
5	ОН	3.5	o	84
6	CH ₂ OH Me	3	СНО	95
7	MeCH ₂ OH	3	Ме-СНО	96
8	CH ₃ (CH ₂) ₆ CH ₂ OH	2	CH ₃ (CH ₂) ₆ CHO	87
9	H ₂ C=CHCH ₂ OH	$1/4 = 15 \min$	H ₂ C=CHCHO	96

Table 1. Oxidation of alcohols to aldehydes and ketones with the DABCO-bromine complex

by exposure to light, air or water. It had no offensive odour of bromine or amine.

In conclusion, we have synthesized and characterized by X-ray crystallography, a bromine complex of use as an efficient, non-metallic, air and water stable oxidant. Further work is directed towards broadening the scope and applications of this novel and efficient oxidant.



2. Experimental

2.1. 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 chloroform (100 mL). A yellow solid appeared as the bromine was taken up. The mixture was stirred for an additional 1 h, then the yellow solid was collected by vacuum filtration. Yield 23.12 g (98%), decomp. 160–165 °C.

2.2. Oxidation of alcohols to carbonyl compounds with the DABCO–bromine complex: general procedure

To a suspension of DABCO–Br₂ (0.262 g, 0.166 mol) in dichloromethane (4 mL) and water (2 mL) in a roundbottomed flask, an appropriate amount of the alcohol (1 mmol) in dichloromethane (2 mL) was added. The reaction mixture was stirred at room temperature until the yellow colour of the complex disappeared. The progress of the reaction was monitored by TLC using petroleum ether/ethyl acetate (8:2) as eluent. Upon completion of the reaction, the organic layer was separated. The aqueous layer was washed with dichloromethane $(2 \times 10 \text{ mL})$. The combined organic layer was washed successively with solutions of 1% HCl, 3% sodium bicarbonate and water. The organic layer was dried over MgSO₄, filtered and evaporated to dryness under reduced pressure to afford the pure corresponding carbonyl compound.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet. 2005.07.057.

References and notes

- Fey, T.; Fischer, H.; Bachmann, S.; Albert, K.; Bolm, C. J. Org. Chem. 2001, 99, 8154.
- (a) Carrey, E. J.; Suggs, J. W. Tetrahedron Lett. 1975, 2647; (b) Piancatteli, G.; Scettri, A.; Auria, M. D. Synthesis 1982, 243; (c) Van den Eyned, A.; Mayence, A.; Maquestiau, A. Tetrahedron Lett. 1992, 48, 463; (d) Cainelli, G.; Cardillo, G. Chromium Oxidation in Organic Chemistry; Springer: New York, 1984.
- (a) Mancuso, A. J.; Huang, S. L.; Swern, D. J. Org. Chem. 1978, 43, 2480; (b) Mancuso, A. J.; Brownfan, D. S.; Swern, D. J. Org. Chem. 1985, 50, 2198.
- 4. Dess, D. B.; Martin, J. C. J. Org. Chem. 1983, 48, 4155.

- 5. Hunsen, M. Tetrahedron Lett. 2005, 46, 1651.
- Ahmad, N.; Ali, H.; Van Lier, J. E. *Tetrahedron Lett.* 2005, 46, 253.
- Fatiadi, A. J. In Organic Synthesis by Oxidation with Metal compounds; Mijis, W. J., De Jong, C. R. H. I., Eds.; Plenum Press: New York, 1986, pp 119–260.
- 8. Heravi, M. M.; Ajami, D.; Nooshabadi, M. A. Iran. J. Chem. Eng. 1999, 18, 88.
- 9. Beheshtiha, Y. Sh.; Heravi, M. M.; Sarmad, N.; Hekmat-Shoar, R. J. Chem. Res. 2001, 79.
- Nooshabadi, M. A.; Aghapoor, K.; Tajbakhsh, M.; Heravi, M. M. J. Sci.I.R. *Iran* 2001, *12*, 1.
- Dehkordi, M. B.; Heravi, M. M.; Khosrofar, P.; Ziafati, A.; Ghassemzadeh, M. *Phosphorus Sulfur Silicon* 2004, 179, 2595.
- Dehkordi, M. B.; Heravi, M. M.; Ziafati, A.; Khosrofar, P.; Ghassemzadeh, M. *Phosphorus Sulfur Silicon* 2004, 179, 1493.
- 13. Heravi, M. M.; Hekmat-Shoar, R.; Pedram, L. J. Mol. Catal. A: Chem. 2005, 231, 89.
- 14. Sharafi, T.; Heravi, M. M. Phosphorus Sulfur Silicon 2004, 179, 2437.
- Allwood, B. L.; Moysak, P. I.; Rzepa, H. S.; Williams, D. J. J. Chem. Soc., Chem. Commun. 1985, 1127.