

Polymeric DABCO–bromine complex: a mild oxidant for the preparation of ketones and aldehydes

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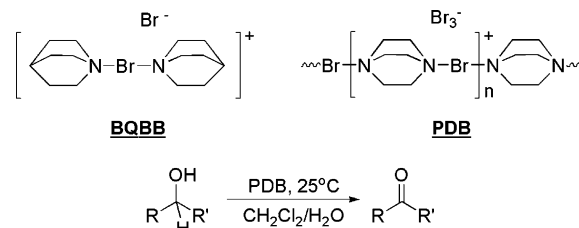
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Abstract—A stable, shelf-ready polymeric oxidant was prepared from the addition of Br₂ to DABCO in CCl₄. This material was used to convert simple primary and secondary alcohols to the corresponding aldehydes and ketones in biphasic CH₂Cl₂/H₂O. © 2006 Elsevier Ltd. All rights reserved.

1. Introduction

Hypervalent halogen complexes have enjoyed a good deal of attention recently as alternatives to Swern,¹ chromate,² and other mild oxidants.³ In particular, the Dess–Martin,⁴ 2-iodoxybenzoic acid (IBX),⁵ and related reagents⁶ have shown a wide range of applications. Herein, we reinvestigate the oxidative properties of a complex prepared by the addition of 2 M equiv of Br₂ to 1,4-diazabicyclo[2.2.2]octane (DABCO) in carbon tetrachloride.⁷ Tetrameric DABCO–bromine complexes prepared in chloroform have been reported and fully characterized.⁸ These complexes contain a linear arrangement of three DABCO subunits in which protonated nitrogen forms hydrogen bonds to nearby nitrogen lone pairs. The source of these hydrogens is unclear, however, it has been suggested that they result ‘from radical oxidation of the solvent by bromine or oxygen’.^{8b} When molecular bromine is added to DABCO in CCl₄, the characteristics of the resulting complex are quite different than those observed for the tetrameric complex. In the absence of a labile hydrogen atom, we feel that the complex is most likely an ionic polymer containing alternating DABCO–bromine–DABCO [N–Br–N]⁺ linkages with Br₃[−] acting as the counter ion.⁹ X-ray crystallography data of a similar complex prepared from quinuclidine (bis(quinuclidine)bromine(I) bromide; BQBB) supports a linear N–Br–N arrangement.⁹ We will, therefore, refer to this material as polymeric DABCO bromine complex, or PDB, throughout the remainder of this letter.

PDB behaves as a stable ionic polymer and is insoluble and unreactive in conventional nonalcoholic organic solvents. However, in the presence of additional DABCO, PDB behaves as a mild oxidant toward simple alcohols. In fact, in the absence of additional DABCO, PDB is entirely unreactive. BQBB has demonstrated increased reactivity in the presence of a pyridinium catalyst in biphasic CH₂Cl₂/H₂O and is selective for the oxidation of 2° alcohols over 1°. ¹⁰ With this in mind, we set out to study the reactivity of the PDB system under BQBB reaction conditions. That is, we investigated (a) the possibility of using a pyridinium catalyst in the absence of additional DABCO, (b) the reactivity of PDB in biphasic CH₂Cl₂/H₂O, and (c) obtain preliminary data regarding the 1°/2° selectivity of PDB by means of a series of oxidations. We plan to explore the utility of PDB in the presence of other reactive functional groups in a forthcoming paper.



2. Results and discussion

Using 2- and 1-pentanol as representative small molecular weight alcohols and PDB as the oxidant, a series of

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Table 1. Oxidation of secondary and primary alcohols using polymeric DABCO–bromine complex in biphasic CH₂Cl₂/H₂O

Entry	Alcohol	Aldehyde or ketone	% Yield of aldehyde/ ketone after 2 and 20 h ^{a,b}	Unreacted alcohol (%) ^{a,b}
1	1-Pentanol	Pentanal	7.3 (41)	84 (54)
2	1-Octanol	Octanal	Trace (31) ^c	93 (64)
3	Isobutyl alcohol	Isobutyraldehyde	6.4 (28)	84 (65)
4	2-Phenylethanol	Phenylethanal	8.7 (27)	80 (55)
5	Benzyl alcohol	Benzaldehyde	29 (85)	63 (14)
6	<i>cis</i> -Hex-2-en-1-ol	<i>cis</i> -Hex-2-enal	97 (92)	0.0 (0.0)
7	2-Pentanol	2-Pentanone	66 (85)	27 (8.3)
8	3-Pentanol	3-Pentanone	68 (89)	24 (0.0)
9	3-Methyl-2-butanol	3-Methyl-2-butanone	64 (86)	29 (0.0)
10	2-Methylcyclopentanol	2-Methylcyclopentanone	54 (97)	38 (trace)
11	3-Methylcyclopentanol	3-Methylcyclopentanone	74 (84)	20 (trace)
12	1-Phenylethanol	Acetophenone	51 (93)	44 (0.0)
13	But-3-en-2-ol	Methyl vinyl ketone	103 (97) ^d	0.0 (0.0)

^a Percent yields and recoveries were determined by GC.

^b Yields and recoveries are given at reaction times of 2 and 20 h (in parentheses).

^c 'Trace' refers to GC signal that was not quantifiable (approximately 0–3%).

^d Values of >100% are indicative of analytical precision: approximately ±3%.

oxidation reactions were performed under conditions identical to those used for the BQBB/PTFA study.¹⁰ Surprisingly, in biphasic CH₂Cl₂/H₂O, PDB is equally reactive when oxidizing 2- and 1-pentanol with or without the pyridinium catalyst. However, very little reactivity is observed under water free conditions. Thus, we postulate that, unlike the BQBB system, PDB oxidations are base promoted. This is evidenced by the reactivity of the oxidant in the presence of additional DABCO under water-free conditions.⁷ Under biphasic conditions, water assumes the role of Bronsted base. These data suggest that the mechanism may be bleach-like in that carbonyl formation relies on an E2 elimination of HX from a hypohalite ester intermediate.

Knowing that no acid catalyst is required, we treated a variety of alcohols with PDB under biphasic CH₂Cl₂/H₂O conditions and examined the mixtures by GC after 2 and 20 h (Table 1). As was observed in the earlier account, the reactions are well behaved with no apparent over oxidation to the carboxylic acid and excellent mass balances.⁷ This study reveals that secondary alcohols generally react faster than primary alcohols (compare entries 1–4 to 7–11; Table 1). Also, allylic alcohols (entries 6 and 13) react very quickly and are entirely oxidized within minutes. Benzylic alcohols (entries 5 and 12) do not appear to be as reactive as allylic substrates although they were somewhat faster than secondary alcohols. Overall, we can assign a preliminary ranking regarding relative rates of oxidation as follows: allylic ≫ benzylic > secondary > primary.

3. Experimental

All oxidations were carried out using PDB prepared in accordance to the earlier precedent.⁷ In a typical reaction, 0.55 mmol PDB (238 mg), 2 mL CH₂Cl₂, 2 mL H₂O, and 1.0 mmol of alcohol were combined in a 5 mL Wheaton[®] V-vial equipped with a spin vane. At the appropriate reaction times (2 or 20 h), 0.5 mmol bromobenzene (internal standard) was added. The organic layer was

removed via Pasteur pipet and the aqueous layer was extracted with three 2 mL portions of CH₂Cl₂. The combined organic layers were diluted to a total volume of 25 mL with CH₂Cl₂ and analyzed by gas chromatography using predetermined response factors.

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