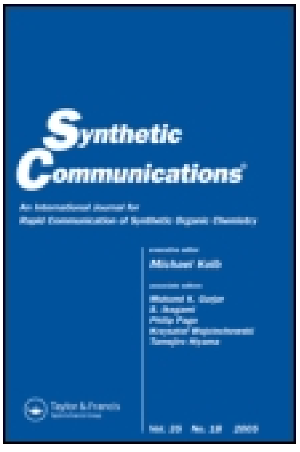

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Efficient Transition-Metal-Free Oxidation of Benzylic and Secondary Alcohols to the Carbonyl Compounds Using an N-Bromosuccinimide/NH_4Cl System

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Efficient Transition-Metal-Free Oxidation of Benzylic and Secondary Alcohols to the Carbonyl Compounds Using an N-Bromosuccinimide/NH_4Cl System

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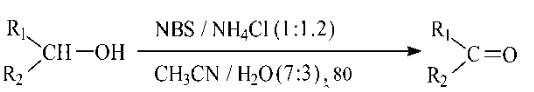
Abstract: The oxidation of a variety of benzylic and secondary alcohols was achieved in excellent yields using an NBS/NH_4Cl system in aqueous acetonitrile (CH_3CN-H_2O; 7/3 v/v) at 80°C under very mild conditions.

Keywords: Oxidation, alcohol, NBS, metal free, ketone

Oxidation of alcohols to the corresponding carbonyl compounds is a valuable transformation in organic synthesis. Many useful reagents and reactions have been developed.[1] In this communication we describe the NBS–NH_4Cl combination as an efficient oxidation reagent (Scheme 1).

A variety of benzylic and secondary alcohols were oxidized to their corresponding carbonyl compounds using N-bromosuccinimide/NH_4Cl in acetonitrile/water (7:3) at 80°C. These results are presented in Table 1. The presence of ammonium chloride (NH_4Cl) was essential for this



Scheme 1.

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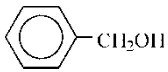
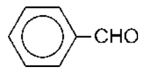
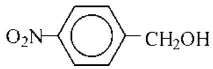
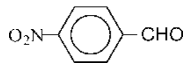
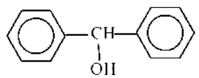
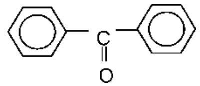
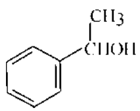
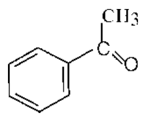
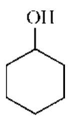
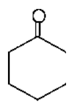
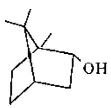
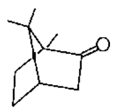
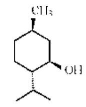
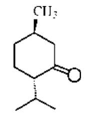
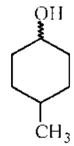
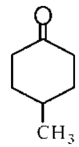
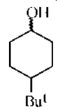
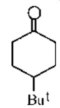
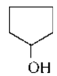
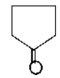
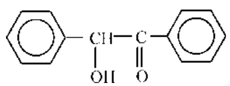
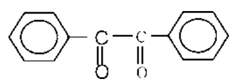
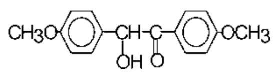
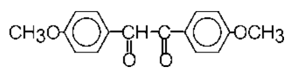
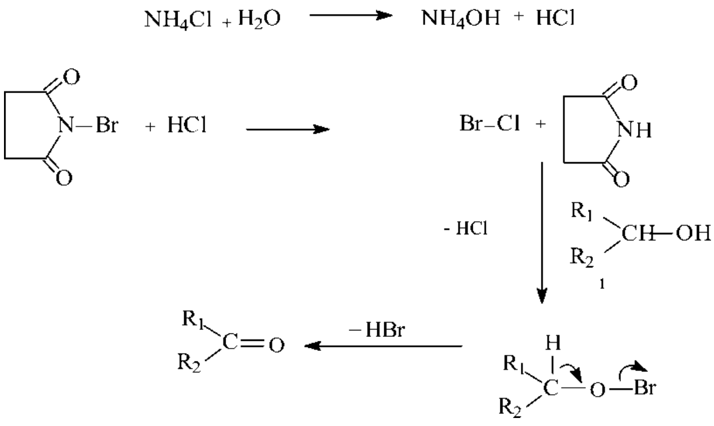
Table 1. Oxidation of alcohols to carbonyl compounds using the NBS–NH_4Cl system[a]

Entry	Substrate	Product	Reaction time (h)	Yield (%)[b]
1			6.0	70
2			6.0	50
3			2.0	92
4			2.5	90
5			2.5	90
6			3.5	75

7			2.5	80
8			3.0	80
9			3.0	75
10			2.0	85
11			1.0	94
12			1.0	92

[a]Reaction conditions: secondary alcohol (1 mmol), *N*-bromosuccinimide (1 mmol), NH_4Cl (1.2 mmol), and CH_3CN-H_2O (7/3 v/v; 5 mL) at 80°C.

[b]Isolated yields.



Scheme 2.

reaction; in its absence, the N-bromosuccinimide alone could not oxidize the cyclohexanol to cyclohexanone. Other ammonium salts such as ammonium acetate were not effective in oxidizing cyclohexanol to cyclohexanone. The mechanism of this reaction is not clear at this stage but perhaps involves the formation of Br-Cl species by the reaction of NBS and NH_4Cl in the aqueous acetonitrile medium, which then reacts with alcohol 1 to afford hypobromite species, which on the abstraction of hydrogen yield the corresponding carbonyl compound as shown in Scheme 2.

In summary, we have developed a simple and convenient system for the oxidation of benzylic and secondary alcohols to carbonyl compounds.

GENERAL EXPERIMENTAL PROCEDURE

N-bromosuccinimide (1 mmol) and NH_4Cl (1.2 mmol) were added to a stirred solution of alcohol (1 mmol) in acetonitrile–water (7/3 v/v; 5 mL). The reaction mixture was heated at 80°C. At the end of reaction, the reaction mixture was extracted with dichloromethane. The combined organic layer was washed with a saturated solution of $NaHCO_3$ and dried over $MgSO_4$. The solvent was evaporated under vacuum, and the residue thus obtained was purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded the corresponding carbonyl compound. The reaction times and yields of the products are given in Table 1.

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1. (a) Backvall, J. *Modern Oxidation Methods*; Wiley-VCH: Verlag, 2004; (b) Ley, S. V.; Madin, A. In *Comprehensive Organic Synthesis*; Trost, B. M. and Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 7, pp. 305–327.