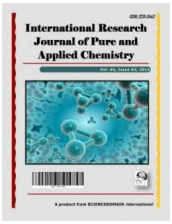

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N-Chloroamines as Oxidants: A Swern-type Oxidation at Room Temperature without Addition of Excess Base

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors designed the study and performed the literature search. Author DK performed the experiments, author RG wrote the manuscript. Both authors read and approved the final manuscript.

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ABSTRACT

A new selective oxidation reaction for the oxidation of alcohols to aldehydes and ketones is described. *N*-Chloramines are used as the oxidant together with dialkylsulfide. This Swern-type reaction can be performed at room temperature without an additional base and the dialkylsulfide may be used catalytically.

Keywords: Oxidation; aldehyde; catalysis.

1. INTRODUCTION

The development of new oxidation methods remains an important target in organic synthesis [1]. One of the problems encountered when searching for such a new reaction is, that many common oxidants are either hard to activate, react unselectively or contain acidic protons, which are not tolerated by many catalysts. Bearing this is mind, it is surprising that

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N-chloroamines, a class of compounds with a high oxidation potential, cheap and easily prepared, while containing no acidic protons, [2] have been virtually unnoticed as oxidants during the last 20 years. We therefore turned our attention towards using *N*-chloroamines as oxidants in various reactions [3]. Here we report our results in using these reagents for the oxidation of alcohols.

Methods most commonly employed for the selective oxidation of alcohols to aldehydes and ketones use either equimolar amounts of highly toxic chromium, [4] are tedious to prepare, like the Dess-Martin reagent, [5] or require an expensive catalyst e.g. the Ley oxidation [6]. More recently oxoammonium-catalyzed oxidations of alcohols have been developed [7]. However, on a laboratory scale the Swern and Pfitzner-Moffat oxidation is still the most commonly employed and very reliable [8]. However this reaction also suffers from some disadvantages, namely the need for low temperature (-78°C) and large amounts of amine. This still holds true for a procedure reported by Corey and Kim, [9] who used *N*-chlorosuccinimide and dialkylsulfide to generate sulfoniumions, the intermediates of the Swern oxidation.

2. EXPERIMENTAL

2.1 N-Chlorodiethylamine

N-Chlorodiethylamine is a known compound and was prepared according to literature-procedures using aqueous sodium hypochlorite [11].

^{1}H-NMR (300MHz, $CDCl_3$): δ = 1.23 (t, 6H, ^{3}J = 6.9Hz); 3.00 (q, 4H, ^{3}J = 6.9Hz) ppm. ^{13}C-NMR (75MHz, $CDCl_3$): δ = 13.1; 58.1 ppm. The data are in accordance with the published data for this compound [11].

2.2 General Procedure for the Oxidation of Alcohols: Oxidation of Isomenthol

To a solution of 469 mg (3.0 mmol) isomenthol in 10 mL dry chloroform 702 mg (4.8 mmol) dibutylsulfide and 1.61 g (15 mmol) *N*-chlorodiethylamine were added under an argon atmosphere. The solution was stirred for 16 h and then poured onto 50 mL water. The layers were separated and the aquous layer washed three times with dichloromethane (30 mL each). The combined organic layers were dried over sodiumsulphate, filtered and the solvent removed in vacuo. From the residue the pure ketone (386 mg, 2.5 mmol, 84%) was isolated by flash-chromatography.

^{1}H-NMR (300MHz, $CDCl_3$): δ = 0.86 (d, 3H, ^{3}J = 6.5Hz); 0.94 (d, 3H, ^{3}J = 6.45Hz); 1.00 (d, 3H, ^{3}J = 6.7Hz); 1.4-1.55 (m, 1H); 1.65-1.8 (m, 2H); 1.90-2.15 (m, 5H); 2.25-2.35 (m, 1H) ppm. ^{13}C-NMR (75MHz, $CDCl_3$): δ = 19.9; 20.9; 21.4; 26.9; 27.0; 29.5; 34.4; 48.1; 57.2; 214.4 ppm. The data are in accordance with the published data for this compound [12].

2.3 Decanal

^{1}H-NMR (300MHz, $CDCl_3$): δ = 0.85-1.67 (m, 17H); 2.24-2.30 (m, 2H); 9.24 (s, 1H) ppm. ^{13}C-NMR (75MHz, $CDCl_3$): δ = 14.1; 22.7; 24.5; 29.1; 29.3; 29.4; 31.8; 31.9; 40.7; 184.9 ppm. The data are in accordance with the published data for this compound [13].

2.4 Benzaldehyde

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.50-7.90 (m, 5H); 10.0 (s, 1H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 129.0; 129.7; 134.4; 136.5; 192.3 ppm. The data are in accordance with the published data for this compound [14].

2.5 Cyclohexylaldehyde

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.85-1.9 (m, 10 H); 2.99 (m, 1 H); 9.40 (s, 1 H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 25.1; 26.0; 26.1; 50.0; 204.8 ppm. The data are in accordance with the published data for this compound [13].

2.6 2-Methylpentanal

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.87-0.92 (t, 3 H, ^{3}J = 7.14 Hz); 1.03-1.08 (m, 3 H); 1.18-1.28 (m, 2 H); 1.51-1.59 (m, 2 H); 2.41-2.53 (m, 1 H); 9.42 (s, 1 H) ppm. The data are in accordance with the published data for this compound [13].

2.7 2,2-Dimethylpent-4-enal

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.06 (s, 6 H); 2.22 (dt, 2 H, ^{3}J = 7.6 Hz, ^{4}J = 1.2 Hz); 5.07 (m, 2 H); 5.70 (m, 1 H); 9.49 (s, 1 H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = = 21.2; 41.5; 45.7; 118.4; 133.1; 205.8 ppm. The data are in accordance with the published data for this compound [15].

3. RESULTS

In our mind, the use of the less reactive *N*-chloroamines as oxidants together with dialkylsulfides could allow the oxidation of alcohols at room temperature and without any additional base, as this is generated *in situ* from the chloroamine. This proved to be correct, as can be seen from the good yield obtained in the oxidation of isomenthol (Fig. 1).

Varying the reaction conditions like the temperature and the solvent did not lead to a higher yield. As in the mechanism reported by Corey and Kim [9] the dialkylsulfide is regenerated, thus catalytic amounts of dialkylsulfide should be sufficient for performing the oxidation. Indeed upon using only 10% of dibutylsulfide menthon was obtained after 3 days in 68% yield, clearly indicating a slow catalytic turnover of the sulfide. We therefore propose - in analogy to the Corey-Kim oxidation [9] - the reaction mechanism depicted in Fig. 2.

In a first step the chloroamine oxidizes the sulfide to the sulfoniumion **A**, [10] in which diethylamine is substituted for the alcohol and sulfoniumion **B** is generated. In analogy to the Swern oxidation this sulfoniumion reacts with the formed diethylamine to the ketone, regenerating the sulfide. The fact that catalytical amounts of sulfide are sufficient for the oxidation supports this mechanism, however to date we were not able to isolate intermediates of the oxidation.

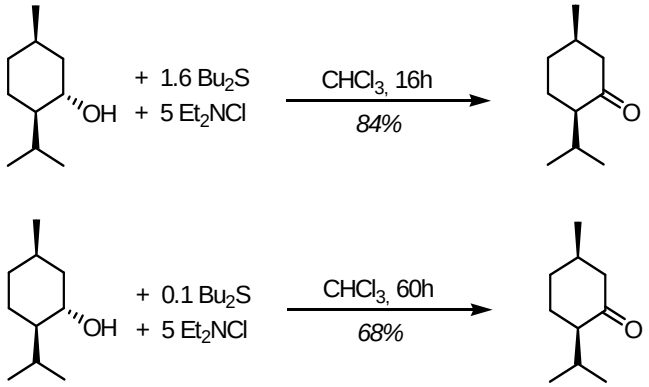


Fig. 1. Oxidati on of isomenthol

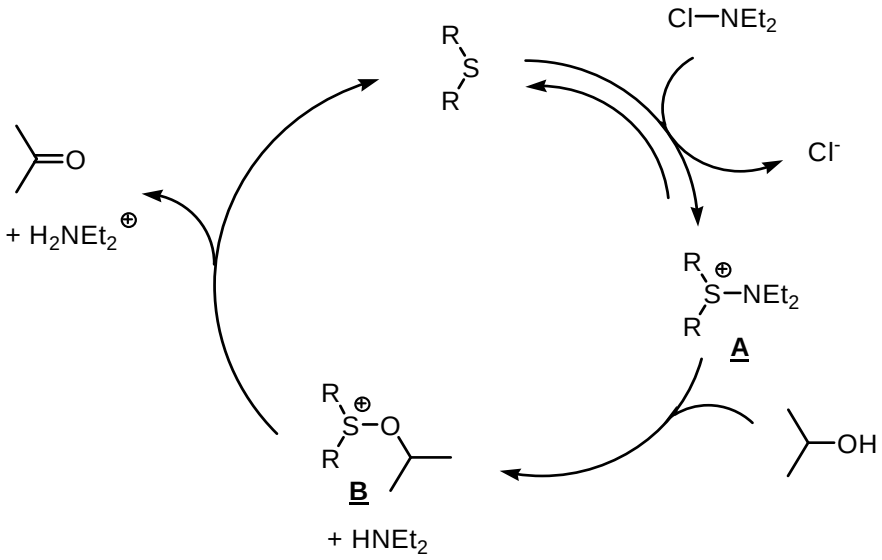
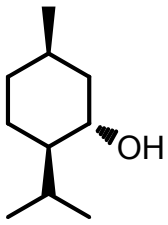
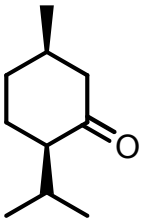
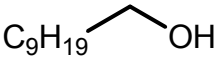
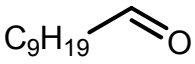
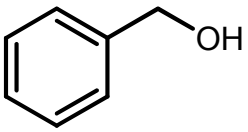
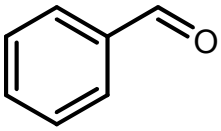
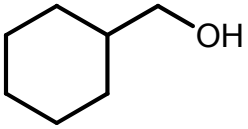
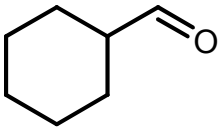
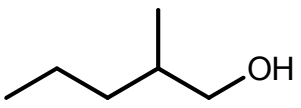
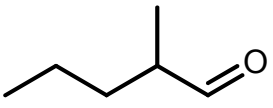
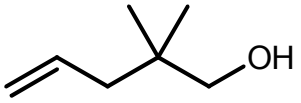
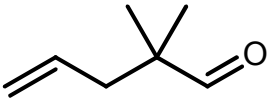


Fig. 2. Proposed reaction mechanism

To check the generality of these simple reaction conditions we oxidized different alcohols using a slight excess of dialkylsulfide. The results are given in Table 1.

As with the Swern oxidation, primary alcohols are oxidized to aldehydes selectively and in moderate to good yields. Products of further oxidation could not be detected. The only byproducts were the corresponding alkylchlorides, arising from a nucleophilic substitution at the carbon of sulfoniumion **B**. Even though in the Corey-Kim reaction this side reaction is a major problem when benzylic alcohols are oxidized. Using our condition a good yield of benzaldehyde is obtained from benzylic alcohol.

Table 1. Oxidation of different alcohols

alcohol	product	yield
		84%
		60%
		53%
		83%
		45%
		68%

Another possible application of our reaction is the formation of enamines from the secondary amine and the aldehydes/ketones. As these might be destroyed during aqueous work-up, we added a large excess of allylic bromide to the reaction mixture after completion of the oxidation for allylation of these enamines. In this reaction we were able to detect only traces of the α-allylated aldehyde. This proves that enamine formation is not, or is only in small amounts, occuring during the reaction using our moderate conditions.

However our reaction conditions could allow the generation of enamines after complete oxidation by azeotropic removal of water. Further studies towards such an interesting cascade reaction are currently beeing performed in our laboratory.

4. CONCLUSION

In summary we have shown for the first time that simple *N*-chloroamines can be used as oxidants in a variation of the Corey-Kim [9] oxidation. In analogy to this reaction we have proposed a mechanism *via* sulfoniumions. The newly developed reaction conditions allow, under laboratory scale, the facile oxidation of primary and secondary alcohols to aldehydes and ketones respectively, in moderate to good yields.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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