

# Oxidation of Alcohols with 1-Decyl-4-aza-1-azoniabicyclo[2.2.2]-octane Chlorochromate under Conventional and Solvent-Free Conditions\*

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**Abstract**—1-Decyl-4-aza-1-azoniabicyclo[2.2.2]octane chlorochromate was proposed as a mild and efficient reagent for oxidation of alcohols to the corresponding carbonyl compounds in boiling acetonitrile or under solvent-free conditions at room temperature. The experimental procedure is simple, and the products are isolated in good to excellent yields.

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Oxidation of organic compounds is one of the most important reactions in modern organic synthesis. Various oxidants have been reported in the literature [1–11]. However, most of them suffer from at least one of the following disadvantages: (1) high cost of preparations, (2) long reaction time, (3) hygroscopicity, (4) high acidity, (5) instability, (6) low selectivity, (7) photosensitivity, (8) dangerous procedures for their preparation, and (9) laborious work-up procedures. Chromium(VI) compounds are the most widely used transition metal oxidants in aqueous solution; their structure depends on the concentration and pH. In dilute solution, monomeric acid chromate ion is present, while dichromate ion predominates as the concentration increases. It is believed that oxidation of alcohols involves intermediate formation of radical species resulting from the substrate reaction with Cr(VI). This scheme also implies participation of Cr(V) derivatives [11].

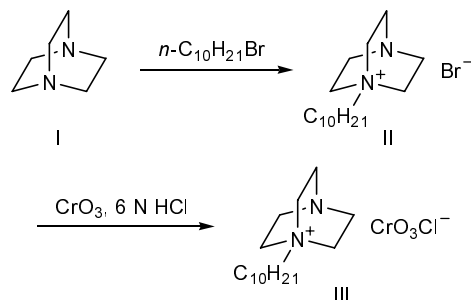
In the recent years, reactions under solvent-free conditions have received increasing attention. The main advantages of these methods, as compared to conventional homogeneous reactions, are greater selectivity, higher rate, simpler experimental procedure, and isolation of purer products [12–26].

In continuation of our studies on the development of efficient reagents for oxidation of organic com-

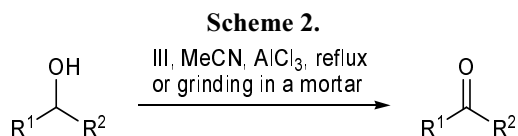
pounds [12–34], in the present article we describe an effective, rapid, mild, and selective procedure for the oxidation of alcohols to the corresponding carbonyl compounds using 1-decyl-4-aza-1-azoniabicyclo[2.2.2]octane chlorochromate (III). This oxidant is readily prepared in high yield by dropwise addition of a solution of chromium(VI) oxide in 6 N hydrochloric acid to an aqueous solution of 1-decyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (II) at room temperature (Scheme 1). The product is filtered off and dried. It is an orange powder which can be stored for several months without loss in activity. Compound III is soluble in acetonitrile, acetone, and dimethylformamide, slightly soluble in chloroform, ethyl acetate, and methylene chloride, and insoluble in carbon tetrachloride, *n*-hexane, and diethyl ether.

Various primary and secondary alcohols were oxidized with reagent III in boiling acetonitrile in the

**Scheme 1.**



\* The text was submitted by the authors in English.



For substrates  $\text{R}^1\text{R}^2\text{CHOH}$ , see Table 1.

presence of  $\text{AlCl}_3$ . As a result, the corresponding carbonyl compounds were isolated in good to excellent yields; for example, benzoin was thus oxidized to benzil in quantitative yield in 90 min (Scheme 2, Table 1). Oxidation of aliphatic alcohols requires a longer reaction time, and the product yields are lower than in the oxidation of benzyl alcohols. The presence of such substituents as  $\text{NO}_2$  or MeO group in the aromatic ring of benzyl alcohols reduces the reaction rate, presumably due to participation of these groups in complex formation with  $\text{AlCl}_3$  (Table 1).

Competing reactions were performed to estimate the selectivity of reagent **III** (Table 2). In the reaction of an equimolar mixture of 2-phenylethanol and benzyl alcohol with 1 equiv of **III**, only benzyl alcohol was oxidized to benzaldehyde (yield 90%), whereas 2-phenylethanol was recovered from the reaction mixture. Treatment of a 1:1 mixture of benzyl alcohol and diphenylmethanol with compound **III** (1 equiv) resulted in quantitative formation of benzophenone. It should be emphasized that in no case overoxidation of carbonyl compounds to carboxylic acids was observed. In the reaction of compound **III** with an equimolar mixture of benzyl alcohol and benzenethiol, benzyl alcohol was selectively oxidized. Likewise, only diphenylmethanol and benzoin were oxidized when equimolar diphenylmethanol–benzaldehyde oxime and benzoin–3-phenyl-2-propen-1-ol mixtures, respectively, were treated with 1 equiv of reagent **III**.

We also performed oxidation of alcohols to carbonyl compounds with 1-decyl-4-aza-1-azoniabicyclo[2.2.2]octane chlorochromate (**III**) under solvent-free conditions. The reactions were carried out by grinding a mixture of an alcohol and compound **III** in a mortar at room temperature. As a result, the corresponding carbonyl compounds were obtained in high yields in a short time. For instance, benzoin was quantitatively converted into benzil in 5 min (Table 1). As compared to the oxidation in boiling acetonitrile, the reaction under solvent-free conditions occurs at a much higher rate and ensures higher yields of the products. In addition, the isolation procedure is much simpler, and no  $\text{AlCl}_3$  is necessary. Estimation of the selectivity in the oxidation of alcohols without a solvent by the com-

peting reaction technique gave almost the same results as those obtained in boiling acetonitrile with the same substrates (Table 2).

Thus 1-decyl-4-aza-1-azoniabicyclo[2.2.2]octane chlorochromate (**III**) is a new efficient reagent for the oxidation of various alcohols to the corresponding carbonyl compounds under mild conditions (in boiling acetonitrile in the presence of  $\text{AlCl}_3$  or without a solvent at room temperature). The proposed reagent is stable and easy to prepare, and it provides high yields of the oxidation products and simple procedure for their isolation.

## EXPERIMENTAL

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian spectrometer at 300 and 75 MHz, respectively, using  $\text{DMSO}-d_6$  as solvent and tetramethylsilane as reference.

**1-Decyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide (II).** 1-Bromodecane, 24.0 g (0.11 mmol), was added under stirring to a solution of 12.0 g (1 mmol) of 1,4-diazabicyclo[2.2.2]octane in 100 ml of acetone. The mixture was heated for 1 h under reflux and cooled, and the precipitate was filtered off, washed with diethyl ether, and dried. Yield 28.5 g (80 %), mp 125–127°C.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.66–3.24 m (12H), 1.48–0.92 m (21H).

**1-Decyl-4-aza-1-azoniabicyclo[2.2.2]octane chlorochromate (III).** 1-Decyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide (**II**), 16.65 g (50 mmol), was dissolved in 50 ml of chloroform, a solution of 5.0 g (50 mmol) of  $\text{CrO}_3$  in 50 ml of 6 N hydrochloric acid was added dropwise under vigorous stirring, and the mixture was vigorously stirred for 20 min at room temperature. The orange precipitate was filtered off, washed with cold distilled water ( $2 \times 50$  ml), and dried in a vacuum desiccator over calcium chloride. Yield 16.14 g (83%); on heating to 126–128°C compound **III** decomposes to give a dark brown material.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.84–3.24 m (12H), 1.66–0.84 m (21H).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 32.66, 30.27, 30.15, 30.05, 29.88, 29.82, 27.18, 26.92, 23.48, 22.69, 22.50, 15.33. Found, %: C 49.29; H 8.73; N 7.28.  $\text{C}_{16}\text{H}_{33}\text{N}_2 \cdot \text{CrO}_3\text{Cl}$ . Calculated, %: C 49.42; H 8.49; N 7.20.

**Oxidation of alcohols with 1-decyl-4-aza-1-azoniabicyclo[2.2.2]octane chlorochromate (III) in boiling acetonitrile (general procedure).** Compound **III**, 0.39 g (1 mmol), and  $\text{AlCl}_3$ , 65.1 mg (0.16 mmol), were added to a solution of 1 mmol of the correspond-

**Table 1.** Oxidation of alcohols with 1-decyl-4-aza-1-azoniabicyclo[2.2.2]octane chlorochromate (**III**) in boiling acetonitrile in the presence of AlCl<sub>3</sub> and under solvent-free conditions<sup>a</sup>

Alcohol	Reaction in acetonitrile		Reaction without a solvent	
	time, h	yield, <sup>b</sup> %	time, min	yield, <sup>b</sup> %
Benzyl alcohol	0.5	98	6.0	95
4-Nitrobenzyl alcohol	1.5	85	17.0	98
3,4-Dimethoxybenzyl alcohol	1.5	95	2.0	90
1-(4-Biphenyl)ethanol	2.0	98	3.0	98
2-Pyridylmethanol	2.0	91	6.0	94
1-Phenylethanol	1.0	98	4.0	95
4-Methoxybenzyl alcohol	1.5	98	2.0	99
2-Methoxybenzyl alcohol	1.8	99	2.0	99
Diphenylmethanol	0.8	100	3.0	100
3-Methoxybenzyl alcohol	1.8	99	5.0	99
4-Chlorobenzyl alcohol	1.0	95	7.0	95
2-Chlorobenzyl alcohol	1.0	94	4.5	88
1,2-Diphenylethanol	1.5	93	4.5	95
1-(4-Bromophenyl)ethanol	2.0	94	5.0	99
1-(4-Chlorophenyl)ethanol	1.3	96	1.5	85
Benzoin	1.5	100	5.0	100
2,3-Dimethoxybenzyl alcohol	1.4	99	3.0	93
Cyclohexanol	2.3	97	4.0	90
1,2,3,4-Tetrahydronaphthalen-1-ol	1.0	98	1.5	93
<i>n</i> -Heptanol	2.5	88	4.5	75
<i>n</i> -Pentanol	2.5	90	4.5	78
L-Menthol	2.5	89	20.0	92
1-Indanol	2.2	94	3.0	89
9-Fluorenol	2.0	91	4.0	88
<i>trans</i> -4-Decylcyclohexanol	2.5	93	4.5	87
2-Naphthylmethanol	1.5	96	2	92
2-Phenylethanol	2.0	89	20.0	75
3-Methylcyclohexanol	2.0	90	4.0	88
1-(4-Methylphenyl)ethanol	1.2	94	1.5	98
3-Phenylpropan-1-ol	2.0	90	20.0	88
Cyclooctanol	2.2	94	15.0	85
Adamantan-2-ol	2.3	92	15.0	94
Geraniol	2.0	91	10.0	88
3-Phenyl-2-propen-1-ol	2.0	96	20.0	85
2-Nitrobenzyl alcohol	2.0	92	15.0	85
2-Hydroxy-5-nitrobenzyl alcohol	2.2	91	8.0	92
(4-Chlorophenyl)phenylmethanol	2.8	94	10.0	90
1-(4-Chlorophenyl)ethanol	2.5	96	20.0	92

<sup>a</sup> The products were identified by comparing with authentic samples (IR, NMR, and TLC data) [11–13].<sup>b</sup> Yield of the purified product.

**Table 2.** Competing oxidation of alcohols with 1-decyl-4-aza-1-azoniabicyclo[2.2.2]octane chlorochromate (**III**) in boiling acetonitrile in the presence of AlCl<sub>3</sub> and under solvent-free conditions

Substrate	Product	Reaction in acetonitrile		Reaction without a solvent	
		time, h	yield, %	time, min	yield, %
PhCH <sub>2</sub> CH <sub>2</sub> OH + PhCH <sub>2</sub> OH	PhCHO	30	90	10	95
PhCHOHPh + PhCH <sub>2</sub> OH	PhCOPh	30	100	5	100
PhSMc + PhCH <sub>2</sub> OH	PhCHO	30	90	10	95
PhCHOHPh + PhCH=NOH	PhCOPh	180	92	10	95
PhCHOHCOPh + PhCH=CHCH <sub>2</sub> OH	PhCOCOPh	90	95	10	95

ing alcohol in 5 ml of acetonitrile, and the mixture was heated under reflux until the initial alcohol disappeared (according to the TLC data; cyclohexane–ethyl acetate, 9:1). When the reaction was complete, the mixture was cooled to room temperature and filtered through a small layer of silica gel, the sorbent was washed with 15 ml of acetonitrile, the filtrate was combined with the washings and evaporated, and the residue was purified by column chromatography on silica gel using ethyl acetate–hexane (10:90) as eluent. The yields of pure carbonyl compounds were 85–100% (Table 1).

**Oxidation of benzyl alcohol with 1-decyl-4-aza-1-azoniabicyclo[2.2.2]octane chlorochromate (**III**) under solvent-free conditions.** A mixture of 0.39 g (1 mmol) of 1-decyl-4-aza-1-azoniabicyclo[2.2.2]octane chlorochromate (**III**) and 0.11 g (1 mmol) of benzyl alcohol was ground in a mortar at room temperature. The progress of the reaction was monitored by TLC, following disappearance of the initial alcohol. When the reaction was complete, the mixture was treated with cyclohexane and filtered. The filtrate was evaporated under reduced pressure, and the crude product (benzaldehyde) was purified by flash chromatography on silica gel using ethyl acetate–hexane (10:90) as eluent. The other alcohols were oxidized in a similar way (Table 1).

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