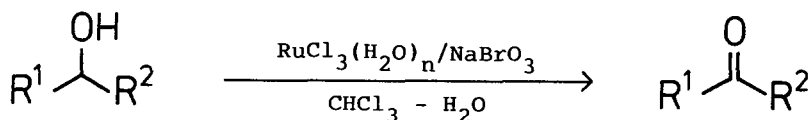


## RUTHENIUM-CATALYZED OXIDATION OF ALCOHOLS WITH SODIUM BROMATE

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*Summary: Ruthenium trichloride-catalyzed oxidation of secondary alcohols with sodium bromate under basic conditions affords ketones in the excellent yields.*

In recent years, numbers of catalyst-oxidant systems involving ruthenium salt as catalyst have extensively been developed to overcome the disadvantage of handling of ruthenium tetroxide which is one of the most powerful oxidising agents for alcohols and olefins. Sharpless reported that  $\text{RuCl}_3(\text{H}_2\text{O})_n/\text{IO}_4^-/\text{H}_2\text{O}-\text{CCl}_4-\text{CH}_3\text{CN}$  system was convenient and efficient for the oxidation of alcohols, ethers, and aromatic rings.<sup>1</sup> Balavoine showed that such system could be applicable to the epoxidation of olefins by the addition of bipyridine to moderate the oxidising power of  $\text{RuCl}_3/\text{IO}_4^-$  system.<sup>2</sup> Iodosylbenzene has been shown to be a effective oxidant for alcohols and aldehydes by Müller.<sup>3</sup> These catalyst-oxidant systems are useful, however, sodium periodate and iodosylbenzene are fairly expensive reagents. We describe herein a convenient and effective method of the oxidation of secondary alcohols to ketones by using readily available sodium bromate ( $\text{NaBrO}_3$ ) in the presence of the catalytic amount of ruthenium trichloride hydrate.



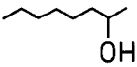
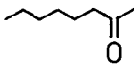
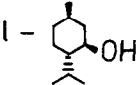

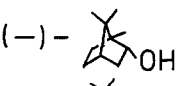

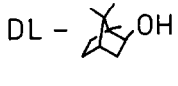


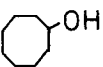





The reaction was conducted in the biphasic solution of chloroform and water in the presence of phase transfer catalyst.

A representative experiment is as follows. A flask was charged with a magnetic stirrer, 3.4 mg (0.5 mol%) of ruthenium trichloride hydrate, 24 mg (0.06 mmol) of Aliquat® 336, 15 ml of chloroform, 645 mg (1.8 mmol) of disodium orthophosphate dodecahydrate, and 7.5 ml of water. The mixture was stirred for a few minutes. Then 390 mg (3 mmol) of 2-octanol and 906 mg (2.0 equiv) of sodium bromate were added to the biphasic solution. The entire reaction mixture was stirred vigorously at room temperature. Consumption of 2-octanol in the reaction was monitored by means of gas chromatography. After charged 2-octanol was completely consumed by stirring for 4.5 h, the reaction mixture was poured into water. Then 20 ml of chloroform was added, and the

phase were separated. The aqueous phase was extracted with three portions of 20 ml of chloroform. The combined extract was dried over anhydrous magnesium sulfate. Filtration, removal of solvent under reduced pressure, followed by purification of the residual oil by column chromatography on silica gel afforded 316 mg (82%) of 2-octanone. Selected examples of the reaction are shown in Table 1.

Table 1 Ruthenium-Catalyzed Oxidation of Alcohols with Sodium Bromate

Entry	Alcohols	Reaction Time (h)	Products	Isolated Yield (%)
1		7.5		100 <sup>a)</sup>
2		4.5		82
3		15.2		95
4		10.4		96
5		9.5	∥	87
6		5.8		75
7		3.1		92
8		5.0		98

a) Determined by means of GLC

Regardless of stereochemistry of hydroxy groups, *endo*- or *exo*-, the oxidation proceeded smoothly (entry 4 and 5). The reaction should be conducted under basic conditions, otherwise bromoketone forms as by-product. The oxidation of *sec*-phenethyl alcohol under acidic conditions (pH 4.5) afforded acetophenone (74%) and  $\alpha$ -bromoacetophenone (23%).

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