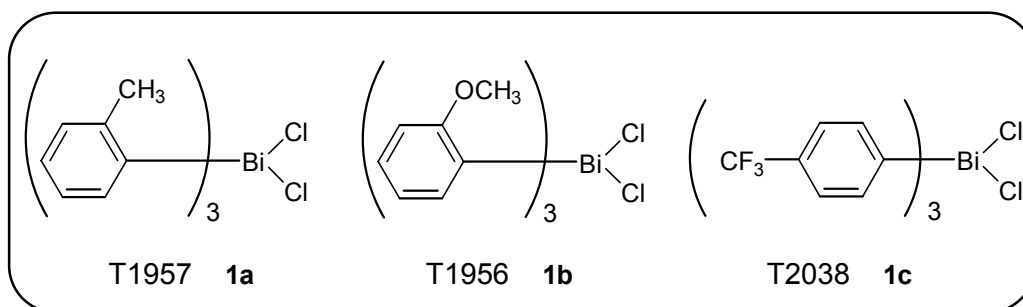


## New Organobismuth Compounds

-for Oxidation of Alcohols-



Triarylbi(dichloride)s are pentavalent organobismuth compounds, and are useful reagents for the oxidation of alcohols to aldehydes and ketones under mild conditions.

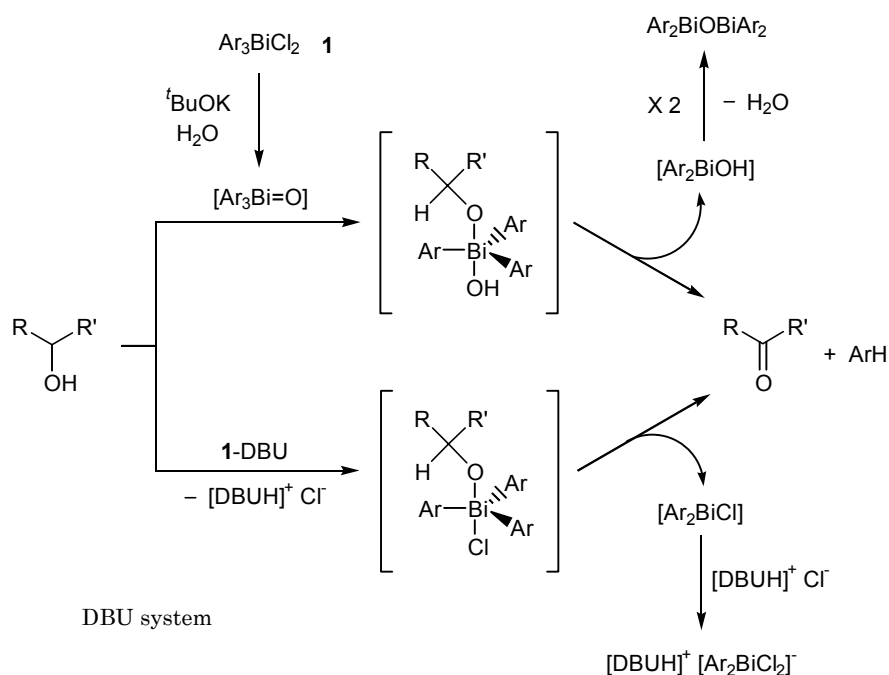
The reaction where primary and secondary alcohols are oxidized to aldehydes and ketones, respectively, is one of the most important reactions in organic synthesis. The most widely known oxidants to date are chromium oxides represented by the Jones reagents, Sarett reagents and Collins reagent, the Dess-Martin periodinane, which is a hypervalent organoiodane, and the Swern oxidation using activated DMSO. Each oxidant, however, has one or more potential drawbacks. For example, chromium oxide is highly toxic, the Dess-Martin periodinane is potentially explosive, and in the Swern oxidation the intermediates are unstable and the by-product, dimethyl sulfide, is a stench.

On the other hand, hypervalent organobismuth compounds are known for their oxidizing ability, derived from the Bi(V)/Bi(III) redox process, and the low toxicity of bismuth, for which they are attracting much attention as oxidants. For example, Challenger *et al.* reported that triphenylbismuth dihydroxide can oxidize alcohols to their corresponding aldehydes and ketones.<sup>1)</sup> And, Barton *et al.* and Dodonov *et al.* independently oxidized alcohols to their corresponding carbonyl compounds using  $(\text{Ph}_3\text{BiCl})_2\text{O}^{2)}$  and  $\text{Ph}_3\text{Bi}(\text{OAc})_2^{3)}$ , respectively, under neutral or basic conditions. However, these methods required long reaction times and high reaction temperatures to obtain the desired products in high yields.

Recently, Matano *et al.* reported that pentavalent organobismuth compound **1** can oxidize alcohols to aldehydes and ketones in the presence of a base under mild conditions.<sup>4)</sup> Accordingly, using **1**, the corresponding aldehydes and ketones can be obtained from various alcohols nearly quantitatively, at room temperature in the presence of  $t\text{-BuOK}$  or 1,8-diazabicyclo[5.4.0]undeca-7-ene (DBU) as a base. It is a highly practical oxidant because of its stability, which affords room temperature storage in spite of its high reactivity. The reaction mechanism is depicted in Scheme 1.

2006. Sep., R-5062E

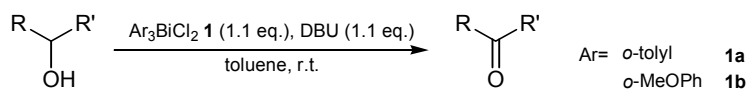
<sup>t</sup>BuOK system



Scheme 1. Plausible reaction mechanisms for the oxidation of alcohols by the <sup>t</sup>BuOK and DBU systems.

In the system using <sup>t</sup>BuOK as a base, **1** reacts with <sup>t</sup>BuOK and H<sub>2</sub>O to form triarylbi-muth(V) oxide or triarylbi-muth(V) hydroxide. This acts as the oxidant, and the alcohol is oxidized in nearly quantitative yield. In the system using DBU as a base, Ar<sub>2</sub>BiCl, which is produced as a by-product in the reaction, reacts with coexisting [DBUH]<sup>+</sup>Cl<sup>-</sup> to form a [DBUH]<sup>+</sup>[Ar<sub>2</sub>BiCl<sub>2</sub>]<sup>-</sup> salt. This salt can be removed by filtration due to its insolubility in organic solvents. Therefore, purification of the reaction product can be easily carried out. Reaction examples of the **1**/DBU system are shown below. (Table 1)

Table 1. Oxidation of alcohols using the Ar<sub>3</sub>BiCl<sub>2</sub> **1**/DBU system in toluene.



When **1a** was used.

Entry	Alcohol	time (h)	Y. (%)
1		0.5	94
2		0.5	> 99
3		0.5	94
4		32	98

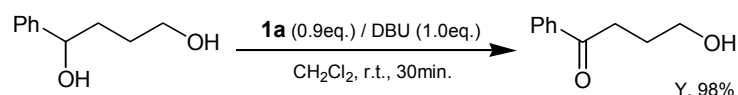
As seen in Table 1, when **1a** was used, the corresponding aldehydes and ketones were obtained from various alcohols in high yields at room temperature. Note that complete stereochemical retention was observed for the oxidation of geraniol. (Entry 3) For trifluoromethyl carbinols, of which oxidation is known to be very difficult, it is also possible to oxidize to the corresponding carbonyl compounds in high yields if a longer reaction time is taken, as demonstrated in Entry 4.

The competition reaction of conjugated alcohols and unconjugated alcohols in the **1a**/DBU system is also reported. Selective oxidization of conjugated alcohols is seen in systems using equimolar conjugated alcohols and ethanol. This selectivity was found to be higher than with the Dess-Martin periodinane. (Table 2)

Table 2. Competitive oxidation of alcohols by **1a** and Dess-Martin periodinane.

RR'CHOH	Ratio of R'R''=O to MeCHO	
	<b>1a</b> / DBU	Dess-Martin
	98:2	91:9
	96:4	90:10
	95:5	75:25

Furthermore, it was also shown that benzylic hydroxyl groups are selectively oxidized, as shown below, for the intramolecular competition reaction using a diol (Scheme 2).



Scheme 2. The intramolecular competitive oxidation of alcohol by the **1a**/DBU system.

In conclusion, **1** can be utilized under milder conditions for the oxidation of alcohols, compared to traditional oxidation methods. **1** is stable at room temperature, and bismuth is considered to be an element of low toxicity. Therefore, **1** is a very useful oxidant for alcohols, and is easily handled.

T1957	Tri- <i>o</i> -tolylbismuth Dichloride	(1a)	5g	1g
T1956	Tris(2-methoxyphenyl)bismuth Dichloride	(1b)		1g
T2038	Tris(4-trifluoromethylphenyl)bismuth Dichloride	(1c)		1g

#### References

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