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A FACILE OXIDATIVE LACTONIZATION OF 1,ω-DIOLS WITH SODIUM BROMITE

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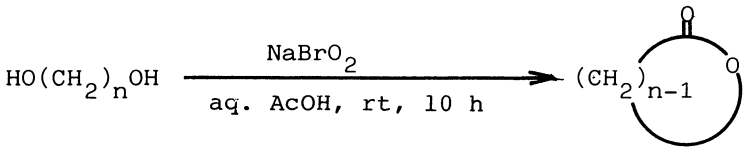
A practically useful method for the oxidation of 1,ω-diols to lactones is described. The scope and limitations are also presented.

Although sodium bromite ($NaBrO_2$) has been used in the industrial field as a desizing agent for textile,[1] its chemistry as a reagent in organic synthesis has been hitherto completely unexplored in comparison with sodium hypohalites (NaOX), iodate ($NaIO_3$), periodate ($NaIO_4$), or related species.

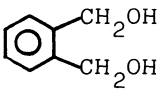
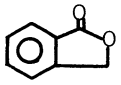
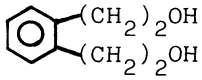
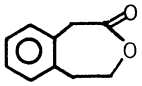
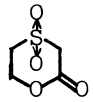
We wish to report here a synthetically useful method for the oxidative lactonization of 1,ω-diols with sodium bromite under mild conditions.



1 2

Thus, we found that 1,ω-diols were oxidized with sodium bromite (three eq.) in aqueous acetic acid at room temperature to afford the corresponding lactones in good yield (Table 1).

Table 1. Oxidative lactonization of diols

	Diol (1)	Product (2)	Yield (%)[a]	Bp(°C/mmHg) or Mp(°C)
a	$HO(CH_2)_4OH$		92	84/12
b	$HO(CH_2)_5OH$		98	88.5/4
c	$HO(CH_2)_6OH$		84	97/15
d			96	73/74
e			85	165-166
f	$S(CH_2CH_2OH)_2$[b]		86	175-176
		$SO_2(CH_2CH_2OH)_2$	12	57-58
g	$HO(CH_2)_2CH(OH)CH_3$	$HO(CH_2)_2\overset{\overset{O}{\|}}{C}CH_3$	83	79/30

[a] Isolated yield. [b] Ten equivalents of $NaBrO_2$ were employed

As shown in the Table 1, the oxidation is generally successful for the 1,ω-diols. Hydroxy-sulfide (1f) gave a sulfonyl lactone (2f), whereas silver carbonate-celite oxidation of 1f has been reported to give lactone (3) only in 9% yield.[2]

(3)

A diol containing secondary hydroxyl group (1g), however, gave hydroxy-ketone (2g).

In order to characterize the reactivity of sodium bromite, we examined the oxidation of 1,5-dihydroxypentane (1b) with related active bromine species under similar conditions (Table 2).

Table 2. Oxidation of 1,5-dihydroxypentane with active bromine compounds.

Reagent	Product	Yield(%)	Reagent	Product	Yield(%)
Br_2		10	$NaBrO_2$		98
	$HOCO(CH_2)_3COOH$	23			
NaBrO		48	$NaBrO_3$	———	——[a]
	$HOCO(CH_2)_3COOH$	15			

[a] The diol (1b) was recovered almost quantitatively.

The lactone (2b) was obtained in only low yield in the case of bromine and sodium hypobromite. Among all only sodium bromite gave a satisfactory result. Moreover, the present lactonization is characteristic to sodium bromite, i.e., no induced species such as Br_2 or NaBrO are involved in the present lactonization, since glutaric acid was not detected in the reaction using $NaBrO_2$.

A most typical reagent for the oxidative lactonization is Fetizon's reagent (silver carbonate on celite).[2] However, is the reaction requires the large excess of expensive silver carbonate (15-25 mole of Ag_2CO_3 per one mole of diol). In view of the simple procedure and also the cheap supply of sodium bromite as an industrial product, the present reaction offers the practically useful method for the oxidative lactonization, especially, in larger scale.

As anticipated, primary monoalcohols produced the oxidative esterification[3] products in good yield under similar conditions (Table 3).

$$2\ RCH_2OH \xrightarrow[\text{aq. AcOH, rt, 5 h}]{NaBrO_2} RCOOCH_2R$$

Table 3. Oxidation of primary alcohols

Alcohol	Product	Yield (%)[a]
$CH_3(CH_2)_3OH$	$CH_3(CH_2)_2COO(CH_2)_3CH_3$	71
$CH_3(CH_2)_4OH$	$CH_3(CH_2)_3COO(CH_2)_4CH_3$	94
$CH_3(CH_2)_5OH$	$CH_3(CH_2)_4COO(CH_2)_5CH_3$	96
$CH_3(CH_2)_7OH$	$CH_3(CH_2)_6COO(CH_2)_7CH_3$	83
$C_6H_5(CH_2)_2OH$	$C_6H_5CH_2COO(CH_2)_2C_6H_5$	91
$C_6H_5CH_2OH$	C_6H_5CHO	84

[a] Isolated yield.

A general procedure is as follows.[4] To a solution of 1,ω-diol (10 mmol) in acetic acid (2 ml), was added dropwise an aqueous solution of $NaBrO_2$ (90% purity, 30 mmol) in water (10 ml) during 30 min at room temperature. After stirring for 10 h, the mixture was treated with saturated aqueous sodium bicarbonate solution, and then with 10% aqueous sodium bisulfite solution (20 ml), and extracted with dichloromethane (20 ml X 4). The crude product was purified by column chromatography on silica gel eluted with dichloromethane to give pure lacton (2).

We thank Nippon Silica Co. Ltd., for gift of anhydrous solid sodium bromite.

References

1) R. Freytag, Textil-Randshaw, 15, 579 (1960).

2) M. Fetizon, M. Goldfier, and J. M. Louis, Tetrahedron, 31, 171 (1975).

3) The oxidative esterification of alcohols was carried out using trialkyltin alkoxide - N-Bromosuccinimide, or calcium hypochlorite, and or bromine - potassium bromate.
T. Ogawa and M. Matsui, J. Am. Chem. Soc., 98, 1629 (1976); S. O. Nwaukwa and P. M. Keen, Tetrahedron Lett., 23, 35 (1982); L. Farkas and O. Shächter, J. Am. Chem. Soc., 71, 2827 (1949).

4) The structure of all products obtained here was fully confirmed by comparison of the physical and spectral date with those of authentic samples.

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