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CONVENIENT SYNTHESIS OF LACTONES BY THE REACTION OF DIOLS WITH N-HALOAMIDES

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Abstract: Reaction of 1,4-butanediol or 1,5-pentanediol with N-haloamides such as N-chlorosuccinimide, N-bromosuccinimide, N-bromoacetamide, isocyanuric chloride, and N,N-dichlorobenzenesulfonamide under mild conditions gave γ-butyrolactone or δ-valerolactone, respectively, in high yields.

Many methods of oxidative lactonization of diols have been developed. These methods consist of the use of reagents such as manganese dioxide,[1] silver carbonate on Celite,[2] ruthenium complexes,[3-6] palladium complexes,[7] bromine with nikel benzoate,[9] sodium bromite,[10] oxonium salts,[11] hydrogen peroxide with heteropoly acids,[12] and quaternary ammonium polyhalides.[13] We have recently shown that the reaction of trichloromelamine with 1,4-butanediol and 1,5-

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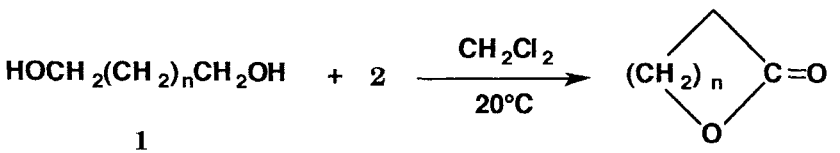
pentanediol afford γ-butyrolactone and δ-valerolactone, respectively, in good yields.[14] Compared with above methods, this method is quite usefull because of the simple procedure, mild conditions, and low cost.

Trichloromelamine can be viewed as a positive halogen compound due to the strong electron withdrawing character of 1,3,5-triazine ring. Therefore, it is of interest to examine the reaction of other compounds which are known source of positive halonium species. However, surprisingly, there are few reports concerning the reaction of diols with N-haloamides,[15] although N-haloamides are well known as oxidants of alcohols. In this paper, we describe the simple oxidative lactonization of diols with N-halosuccinnimides and their derivatives.

When 1,4-butanediol (**1a**) was allowed to react with N-chlorosuccinimide (**2**) as a representative N-haloamides in methylene chloride at room temperature for 5 h, γ-butyrolactone (**3a**) was produced in 88 % yield (Table 1).



1 **3**

1, 3	n
a	2
b	3

This reaction also proceeded in chloroform, carbon tetrachloride, acetonitrile, and benzene. However, pyridine which is known as a good solvent for oxidation of alcohols[15] was not suitable in this reaction. δ-Valerolactone (**3b**) was also obtained from the corresponding diol, 1,5-pentanediol (**1b**). Lactones of four - or seven-membered rings were not produced from the corresponding diols.

Table 1. Reaction of diols (**1**) with NCS (**2**) at 20°C

Diol	Ratio of **2**:**1**[a]	Solvent	Time (h)	Product	Yield[b] (%)
1a	2	CH_2Cl_2	10	**3a**	49
1a	3	CH_2Cl_2	5	**3a**	88
1a	4	CH_2Cl_2	5	**3a**	86
1a	3	$CHCl_3$	5	**3a**	62
1a	3	CCl_4	5	**3a**	15
1a	3	CH_3CN	5	**3a**	58
1a	3	Benzene	5	**3a**	32
1a	3	Pyridine	10	**3a**	0
1b	3	CH_2Cl_2	5	**3b**	91
1b	3	Pyridine	10	**3b**	0

[a] Refers to mol/mol. [b] Determined by GC analysis.

Next, in order to extend this oxidative lactonization method, the reaction of other N-haloamides with **1a** was examined. The results

are shown in Table 2. N-Haloamides such as N-bromoacetamide, isocyanuric chloride, N,N-dichlorobenzenesulfonamide reacted readily at room temperature to afford **3a** in moderate to high yields. Although the mechanism is not clear at present, these are probably formed by the way of the hemiacetal, as in the case of diol oxidation by trichloromelamine,[14] because the corresponding carboxylic acid was not detected in the reaction mixture.

Table 2. Reaction of 1,4-butanediol (**1a**) with several N-haloamides in methylene chloride at 20°C for 5 h

N-Haloamides	Ratio of N-haloamides:**1a**[a]	Yield of **3a**[b] (%)
N-Bromosuccinimide	3	57
N-Bromoacetamide	3	82
Isocyanuric chloride	1	85
N,N-Dichlorobenzenesulfonamide	1.5	80

[a] Refers to mol/mol. [b] Determined by GC analysis.

Experimental Section

N-Chlorosuccinimide (**2**), N-bromosuccinimide, N-bromoacetamide, and isocyanuric chloride were commercially available and used as received. N,N-Dichlorobenzenesulfonamide was prepared by the method reported previously.[16] Starting diols and solvents were purified by distillation. GC (Carbowax 20 M, 10 %, 2 m) was used for separations and yield determinations.

γ-Butyrolactone (3a); Typical Procedure:

To a solution of 1,4-butanediol (**1a**) (900 mg, 10 mmol) in methylene chloride (50 mL) was added N-chlorosuccinimide (**2**) (4.01 g, 30 mmol). The solution was stirred for 5 h at 20°C. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography (Wakogel C-200, eluent: methylene chloride) to give an oil (756 mg). The spectral data of the product agreed with those of an authentic sample of γ-butyrolactone (**3a**).

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