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# SYNTHESIS OF LACTONES VIA THE OXIDATION OF $\alpha, \omega$ -DIOLS WITH SODIUM BROMITE AND ALUMINA UNDER WATER FREE CONDITIONS

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Abstract: Oxidation of  $\alpha, \omega$ -diols with sodium bromite can be readily performed in dichloromethane to afford lactones in fair good yield under mild and neutral conditions with the aid of chromatographic acidic alumina.

Lactones are important subunits in broad range of natural products<sup>1</sup> and are also useful building blocks in organic synthesis. Consequently, in addition to the welldocumentated Baeyer-Billiger oxidations<sup>2</sup> and Fetizon's procedure using celite supported silver carbonate reagents,<sup>3</sup> numerous interesting methodologiess have been developed from synthetic and mechanistic points of view.<sup>4</sup>

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Our recent work on new cleaner chemical processes in nonaqueous media<sup>5-8</sup> have shown that solid support materials such as aluminas,<sup>5</sup> silica gel,<sup>6</sup> clays,<sup>7</sup> and zeolite<sup>8</sup> exhibit remarkable catalysis in the transformation of a variety of functional groups with certain solid reagents which are insoluble in organic solvents. For example, although conventional reactions with sodium bromite have been conducted under aqueous conditions,<sup>9,10</sup> alcohols<sup>5h</sup> and sulfides<sup>7b,8</sup> were readily oxidized to the corresponding sulfoxides and carbonyl compounds, respectively, in dichloromethane with the aid of alumina,<sup>5h</sup> clays,<sup>7b</sup> or zeolite.<sup>8</sup> Moreover, our procedures have proved to be useful for the formation of lactones *via* Baeyer-Billiger oxidation of alicyclic ketones with solid peroxy acid derivatives.<sup>5c,7b</sup> These perspectives prompts us to test an alternative approach to lactone synthesis *via* the dehydrogenation of  $\alpha, \omega$ -diols with an environmentally friendly reagent, sodium bromite (NaBrO<sub>2</sub>, 1), under dry and heterogeneous conditions.

The lactonization was simply accomplished by vigorously stirring a mixture of a diol, chromatographic acidic alumina, 1, and dichloromethanethe at ambient temperature under inert atmosphere. When a diol was added to a stirred mixture of alumina and 1 in  $CH_2Cl_2$  (vide Oxidation Procedures in Experimental Section), the suspension became yellow. After allowing the reaction for 1.5-2 hours, the color turned orange as gently exothermic process took place. The orange color gradually discharged while the exothermic process was decreasingly evident. GC analysis of the colorless reaction mixture showed that no or only a faint trace of the diol was involved. The progress of the reaction could therefore be followed not only roughly by color change of the heterogeneous mixture, but, more conveniently, by GC analysis of the supernatant withdrawn at intervals. After





simple work-up procedure through filtration and solvent removal, pure lactone was isolated by a single chromatographic separation.

Under such conditions, 1,5-pentanediol 2a, for example, was completely consumed after 3 h and gave a crude mixture involving  $\delta$ -valerolactone 3a in 94% GC selectivity, from which pure 3a was isolated in 87% yield. In the absence of the alumina, however, the reaction was sluggish and *ca*. 50% of unchanged 2a was

Entry			Alumina	Time		Yield <sup>b</sup>
No.	Substrate	NaBrO <sub>2</sub> c	(g)	<u>(h)</u>	Products	(%)
1	2a	4	3	3	3a	87
2	2b	3	3	1.5	2ь	85
3	<b>2</b> c	3	3	4	$3c + 4(6:4)^d$	85 <sup>e</sup>
4	2d	2	4	6	3d	88
5	<u>2e</u>	3	2	4	<u>3e</u>	86

Table 1. Synthesis of lactones from diols $^a$ 

a) Conditions: under argon, ambient; substrate 2 0.5 g, CH<sub>2</sub>Cl<sub>2</sub> 20ml. b) Isolated yield based on starting substrate. c) [NaBrO<sub>2</sub>]/[2] (mole ratio). d) Product ratio, 3c vs. 4, determined by NMR. e) Total yield of 3c plus 4.

recovered even after 24 h. Obviously, alumina is essential for the lactonization to be accomplished in a reasonable period of time. The NaBrO<sub>2</sub>/Alumina system was then applied to oxidative dehydrogenation of the related diols **2b-2e**, for which optimum conditions (quantities of 1 and the alumina, and reaction times) were determined on the basis of reactivity of the substrates and selectivity and yield of the lactones. The results are collected in Scheme 1 and Table 1.

In short, the present study has shown that the NaBrO<sub>2</sub>/Alumina system in dichloromethane gives an operationally simple and high-yielding synthesis of lactones, applicable to a number of  $\alpha, \omega$ -diols.

#### **EXPERIMENTAL SECTION**

The <sup>1</sup>H NMR spectra were recorded with a JEOL JNM-FX 60 (60 MHz) spectrometer for solutions in deuteriochloroform using TMS as an internal standard. Analytical gas chromatography was performed on a Shimadzu GC-6A

or GC-4CM instrument with a 2 m x 4mmø column packed with 5% PEG-20M on Chromosorb WAW-DMCS or 1.5% Silicone OV-17 on Shimalite WAW-DMCS, respectively, with temperature programming. Dichloromethane was rigorously dried, distilled, and stored over molecular sieves. Sodium bromite trihydrate, a gift from Nippon Silica Industrial Co., Ltd., and chromatographic acidic alumina (ICN BIOMEDICALS, Alumina A, Super I) were used as received. Commercial chemicals, 1,5-pentanediol **2a**, 3-methyl-1,3,5-pentanetriol **2b**, *cis*-1,2-cyclohexanedimethanol **2d**, and 1,2-benzenedimethanol **2e**, were used without further purification. 2,2-Dimethy-1,5-pentanediol **2c** was prepared by the reduction of 2,2-dimethyglutaric acid with LiAlH<sub>4</sub> in dry ether. The purities of all substrates were checked by GC prior to use.

Oxidation Procedures.— Lactonization of  $\alpha, \omega$ -diols can be easily carrird out by using 2-4 fold excess of sodium bromite and 2-4 g of the alumina per 0.5 g of the substrates. The following procedures for 1,5-pentanediol **2a** is representative. In a 30 mL round-bottom flask were placed the alumina (3 g), NaBrO<sub>2</sub> (19 mmol), and dichloromethane (20 mL), and the mixture was stirred for a few minutes. After adding **2a** (0.5 g, 4.8 mmol; [NaBrO<sub>2</sub>]/[**2a**]= 4) in one portion, the flask was flushed with dry argon and then capped tightly with a glass stopper. The lactonization was conducted by vigorously stirring the heterogeneous mixture at ambient temperature; care should be taken in continuing the efficient stirring during the reaction to ensure smooth reaction and to attain reproducible results. After 3 hours, the whole mixture was transferred onto a sintered glass funnel, and the filter cake was thoroughly washed with portions of dry ether and dichloromethane. The combined clear filtrate was condensed on a rotary evaporator to leave an oil, which was immediately chromatographed on a silica gel column (Merck, Silica Gel 60; chloroform) to afford  $\delta$ -valerolactone **3a** in 87% yield based on starting **2a** (Entry 1).

The other  $\alpha,\omega$ -diols were similarly oxidized with NaBrO<sub>2</sub>/alumina system in dichloromethane for 1.5-6 h at ambient temperature. Common work-up procedure followed by chromatographic separation afforded the indicated products, which were characterized by IR and NMR spectroscopies.

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