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**Registry No.** CH<sub>3</sub>OH, 67-56-1; *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OAc, 830-03-5; CH<sub>3</sub>OAc, 79-20-9; *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OH, 100-02-7; CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CHO, 111-71-7; CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH=CHOAc, 35468-97-4; 4-(methylamino)pyridine, 1121-58-0; *p*-(chloromethyl)styrene polymer, 29296-32-0; 1-methylcyclohexanol, 590-67-0; 1-methylcyclohexyl acetate, 16737-30-7; indole, 120-72-9; 1-acetylindole, 576-15-8; methyl (3 $\alpha$ ,7 $\alpha$ ,12 $\alpha$ )-trihydroxy-5 $\beta$ -cholan-24-oate, 1448-36-8; methyl (3 $\alpha$ ,7 $\alpha$ ,12 $\alpha$ )-triaceoxy-5 $\beta$ -cholan-24-oate, 33744-75-1; 3 $\beta$ -cholest-5-en-3-ol, 57-88-5; 3 $\beta$ -cholest-5-en-3-ol TBDMS ether, 57711-50-9; 3 $\beta$ -(triphenylmethoxy)cholest-5-ene, 51414-56-3.

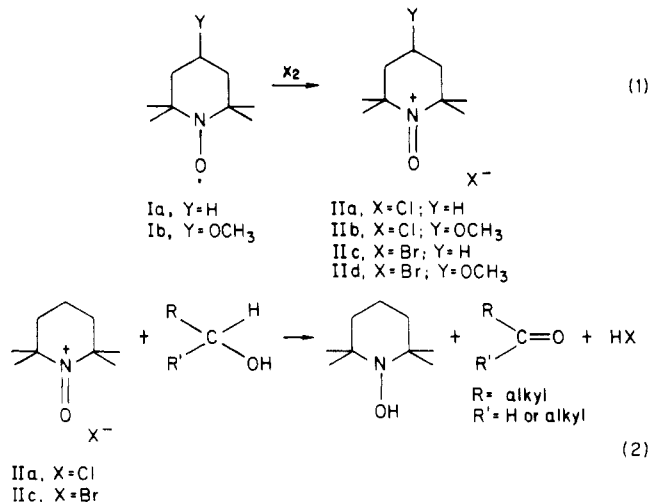
## Oxidation of Diols with Oxoammonium Salts

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2,2,6,6-Tetramethylpiperidine-1-oxyl (Ia) known as a stable radical<sup>1</sup> can be easily oxidized by chlorine or bromine to obtain the corresponding oxoammonium salts (IIa)<sup>2</sup> and (IIc)<sup>3</sup> (eq 1). As shown in eq 2, primary or secondary



alcohols are oxidized to the corresponding carbonyl compounds with IIa or IIc, respectively, and oxoammonium salt itself is reduced to hydroxylamine in the oxidation of alcohols.<sup>4,5</sup> The most recent report of selective oxidation of alcohols by M. F. Semmelhack<sup>6</sup> involves this oxoammonium ion as a mediator for the electrolytic oxidation.

Some oxidative methods are available for the selective oxidation of diols.<sup>7</sup> A most typical reagent for the oxidative lactonization is silver carbonate on Celite<sup>8</sup> (Fetizon's reagent). However, this oxidation requires the large excess of silver carbonate. Other methods using ruthenium<sup>9,10</sup> or

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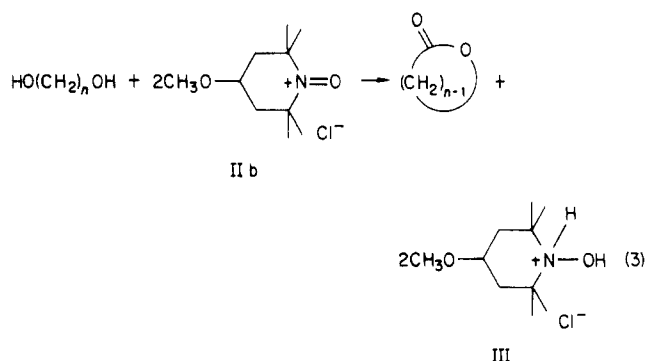
Table I. Oxidation of 1, $\omega$ -Diols with IIb<sup>a</sup>

diol	product	time, min	yield, <sup>b</sup> %	bp, °C/mmHg
HO(CH <sub>2</sub> ) <sub>3</sub> OH		60	trace	
HO(CH <sub>2</sub> ) <sub>4</sub> OH		10	100 (81) <sup>c</sup>	90/24
HO(CH <sub>2</sub> ) <sub>5</sub> OH		30	61 (40) <sup>c</sup>	80/4
HO(CH <sub>2</sub> ) <sub>6</sub> OH		60	trace	

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub> at 25 °C. <sup>b</sup> GLC yield based on the starting alcohol. <sup>c</sup> Isolated yield.

bromine with nickel(II) benzoate<sup>11</sup> or alkanooates<sup>12</sup> have been reported.

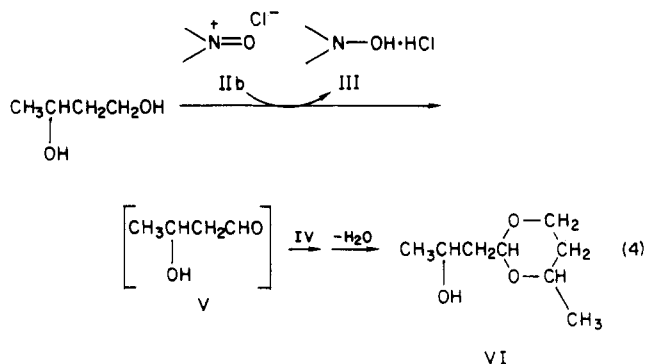
We now report the oxidation of diols with oxoammonium salt IIb under mild conditions. As shown in eq 3, 1, $\omega$ -diols



were oxidized with IIb (2 equiv) in methylene chloride at room temperature to afford the corresponding lactones, and IIb was reduced to the corresponding hydroxylamine hydrochloride (III). As shown in Table I, the oxidation is successful for 1,4-butanediol to afford  $\gamma$ -butyrolactone quantitatively. However,  $\delta$ -valerolactone is obtained in good yield, and the lactones of four- or seven-membered rings are detectable as the trace by GLC.


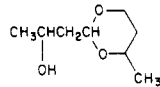
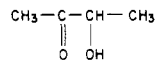
As shown in Table II, 1,4-pentanediol containing primary and secondary hydroxyl groups was oxidized by IIb to give  $\gamma$ -valerolactone in 83% yield and no other carbonyl compounds such as hydroxy ketone or aldehyde were obtained. This result might support the selective oxidation of primary alcohol by IIb.

1,3-Butanediol (IV) was also oxidized by IIb to give acetal VI in quantitative yield (eq 4). As shown in Table



- (10) Ishii, Y.; Osakada, K.; Ikariya, T.; Saburi, M.; Yoshikawa, S.; *Tetrahedron Lett.* 1983, 24, 2677.
- (11) Doyle, M. P.; Dow, R. L.; *Synth. Commun.* 1980, 10, 881.
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Table II. Oxidation of Diols with Iib<sup>a</sup>

diol	product	Iib (eq)	time, min	yield, <sup>b</sup> %	bp, °C/mmHg
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$		1 2 3	5 60 60	17 45 (33) <sup>c</sup> 83	93/18
$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{OH}$		0.5 1 2	5 5 10	53 100 (61) <sup>c</sup> 9	100/7
$\text{CH}_3-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{CH}_3$		1	30	74	

<sup>a</sup> In  $\text{CH}_2\text{Cl}_2$  at 25 °C. <sup>b</sup> GLC yield based on the starting alcohol. <sup>c</sup> Isolated yield.

II, the acetal VI was further oxidized by excess use of Iib to give a complicated mixture. These results might suggest that a primary hydroxyl group was initially oxidized faster than a secondary hydroxyl moiety to give hydroxy aldehyde V as a intermediate. Subsequently V reacts with IV, and dehydration will occur by hydrogen chloride derived from Iib to give VI as shown in eq 4.

2,3-butanediol was selectively oxidized by equimolar Iib to give acetoin in 74% yield, as shown in Table II.

As described above, we found the selective oxidation of alcohols by oxoaminium salt Iib and applied this method to the oxidative lactonization of diols. In view of the simple procedure that requires a mild condition, the present reaction offers the useful method for the oxidative lactonization of limited diols.

### Experimental Section

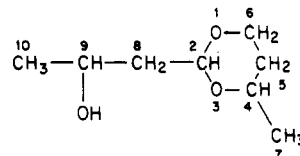
Nuclear magnetic resonance spectra were measured on a JEOL JNM-GX400 FT NMR spectrometer in  $\text{CDCl}_3$  with tetramethylsilane as internal standard. The infrared spectra were measured on a JASCO FT/IR-3. 4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (Ib) and the oxidizing agent Iib were prepared by the method reported previously.<sup>13</sup>

**4-Methoxy-1-oxo-2,2,6,6-tetramethylpiperidinium Chloride (Iib).** Anhydrous chlorine was bubbled into the stirred solution of 2.0 g (10.7 mmol) of Ib in 100 mL of  $\text{CCl}_4$ . The orange precipitate appeared, and it was filtered and washed with  $\text{CCl}_4$  to give 2.1 g (9.5 mmol, 89%) of Iib: mp 121–123 °C dec; IR (KBr) 2951, 2897, 2827, 1616, 1466, 1446, 1388, 1377, 1219, 1161, and 1106  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{10}\text{H}_{20}\text{NO}_2\text{Cl}$ : C, 54.17; H, 9.09; N, 6.32; Cl, 15.99. Found: C, 53.60; H, 9.22; N, 6.29; Cl, 16.88.

**Oxidation of 1,4-Butanediol by Use of Iib.** To a solution containing 2.05 g (22.7 mmol) of 1,4-butanediol in 200 mL of anhydrous methylene chloride was added 10.6 g (47.8 mmol) of Iib under an atmosphere of argon at room temperature. After the reaction was over, the solution was washed with water (200 mL) and dried with anhydrous sodium sulfate. The solvent was evaporated in vacuo. The residue was distilled under reduced pressure to give 1.59 g (18.5 mmol, 81%) of  $\gamma$ -butyrolactone. The physical and spectral data of the obtained product agreed with those of authentic sample of  $\gamma$ -butyrolactone, completely.

**Oxidation of 1,3-Butanediol by Use of Iib.** To a solution containing 4.26 g (47.4 mmol) of 1,3-butanediol in 200 mL of anhydrous methylene chloride was added 10.5 g (47.4 mmol) of Iib under an atmosphere of argon at room temperature. After the reaction was over the solution was washed with water (200 mL) and dried with anhydrous sodium sulfate. The solvent was evaporated in vacuo. The residue was distilled under reduced pressure to give 2.32 g (14.5 mmol, 61%) of 2-(2-hydroxypropyl)-4-methyl-1,3-dioxane (VI): bp 100 °C (7 mmHg); mass spectrum,  $m/e$  160; IR (neat) 802, 895, 1107, 1126, 1168, 1380, 2858, 2932, 2970, and 3458  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\text{CDCl}_3/\text{Me}_4\text{Si}$  int)  $\delta$  1.18 (dd, 3 H,  $J = 6.2$  and 0.6 Hz, H-10), 1.23 and 1.24 (d,  $J = 6.3$  Hz, H-7, diastereoisomer), 1.44–1.48 (m, 1 H, H-5<sub>ax</sub>), 1.63–1.75 (m, 1 H, H-5<sub>eq</sub>), 1.76 (t, 2 H,  $J = 4.8$  Hz, H-8), 2.85–3.04 (s, 1 H,

OH), 3.71–3.81 (m, 2 H, H-4 and H-6<sub>ax</sub>), 4.08–4.13 (, 2 H, H-9 and H-6<sub>eq</sub>), 4.78 (t, 1 H,  $J = 4.8$  Hz, H-2); <sup>13</sup>C NMR ( $\text{CDCl}_3/\text{Me}_4\text{Si}$  int)  $\delta$  21.7 (q, C-7), 23.3 (q, C-10), 32.9 (t, C-5), 43.1 (t, C-8), 64.2 (d, C-9), 66.6 (dd, C-6), 72.9 (d, C-4) 101.0 (d, C-2); determined by off-resonance method. Anal. Calcd for  $\text{C}_8\text{H}_{16}\text{O}_3$ : C, 59.97; H, 10.07. Found: C, 60.11; H, 10.07.



**Oxidation of 1,4-Pentanediol by Use of Iib.** To a solution containing 2.82 g (27.1 mmol) of 1,4-pentanediol in 150 mL of anhydrous methylene chloride was added 12 g (54.2 mmol) of Iib at room temperature. After the reaction was over, the solution was washed with water and dried with anhydrous sodium sulfate. The solvent was evaporated in vacuo. The residue was distilled under reduced pressure to give 900 mg (9.0 mmol) of  $\gamma$ -valerolactone. The physical and spectral data of the obtained product completely agreed with those of authentic sample of  $\gamma$ -valerolactone.

**Registry No.** Iib, 95407-70-8;  $\text{HO}(\text{CH}_2)_3\text{OH}$ , 504-63-2;  $\text{HO}(\text{CH}_2)_4\text{OH}$ , 110-63-4;  $\text{HO}(\text{CH}_2)_5\text{OH}$ , 111-29-5;  $\text{HO}(\text{CH}_2)_6\text{OH}$ , 629-11-8;  $\text{CH}_3\text{CH}(\text{OH})(\text{CH}_2)_3\text{OH}$ , 626-95-9;  $\text{CH}_3\text{CH}(\text{OH})(\text{C}-\text{H}_2)_2\text{OH}$ , 107-88-0;  $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_3$ , 513-85-9;  $\text{CH}_3\text{C}(\text{O})\text{CH}(\text{OH})\text{CH}_3$ , 513-86-0; 2-oxetanone, 57-57-8; dihydro-2-(3H)-furanone, 96-48-0; tetrahydro-2H-pyran-2-one, 542-28-9; 2-oxepanone, 502-44-3; 5-methyldihydro-2(3H)-furanone, 108-29-2;  $\beta$ ,4-dimethyldioxane-2-methanol, 96948-63-9.

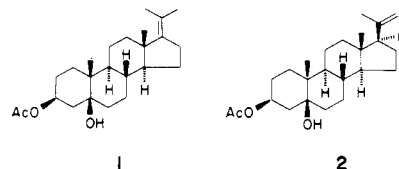
### Preparation and Acid-Catalyzed Rearrangement of a C-17 Isopropylidene and a C-17 Isopropenyl Sterol

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In connection with a study directed toward the biogenetic-type synthesis of 3,5-dioxygenated steroids via acid-catalyzed cyclization of a polyene epoxide,<sup>2</sup> we had interest in preparing steroids 1 and 2 and studying their acid-catalyzed rearrangement.



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