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Oxidation of Diols with Sodium Bromite Trihydrate in Organic Solvents in the Presence of Alumina

Takashi MORIMOTO, Masao HIRANO, Keiko IWASAKI, and Takashi ISHIKAWA

The title oxidation of diols with two primary hydroxy groups (symmetrical diols) and those with both a primary and a secondary hydroxy group (unsymmetrical diols) gives the corresponding lactones or the hydroxy ketones, being dependent upon the types of diols.

Sodium bromite trihydrate 1 (referred to simply as $NaBrO_2$) is a versatile reagent for the oxidative transformation of many classes of organic compounds[1] inclusive of diols[2] in aqueous media, but its behavior in a water-free solvent has not been fully studied.[3] In the course of the work aiming at the oxidation of various functional groups with 1 in aprotic solvents, successful conversion of diols to the corresponding lactones and/or the hydroxy ketones was found in dichloromethane (DM) or acetonitrile (AN) with the aid of alumina under mild conditions.[4]

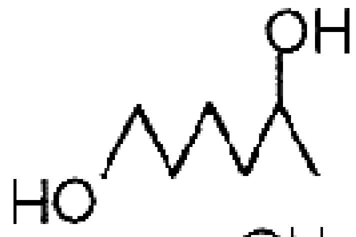
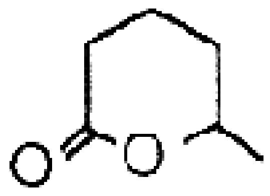
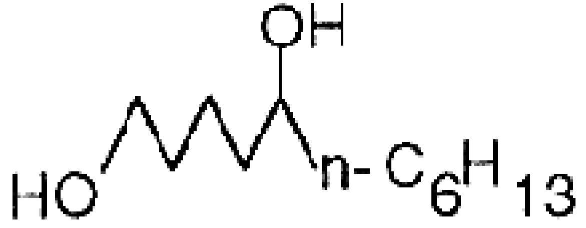
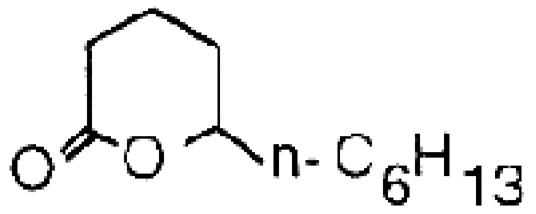
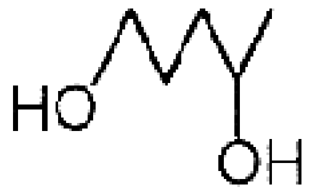
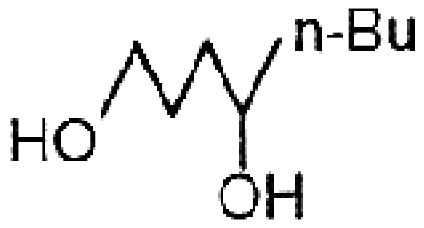
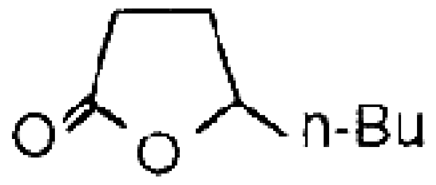
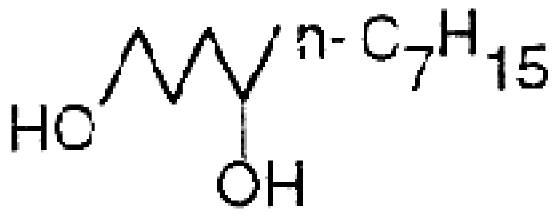
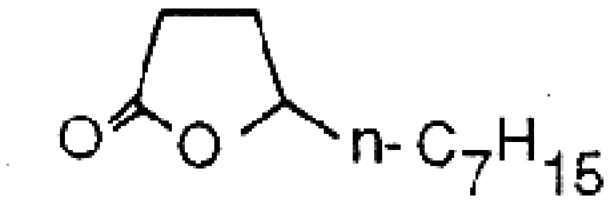
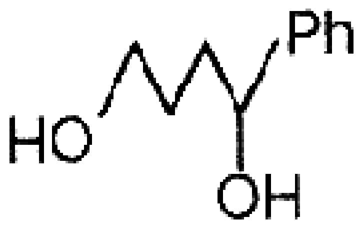
Thus various symmetrical 1,4- and 1,5-diols were treated with the $NaBrO_2$/alumina system in DM at room temperature under anaerobic conditions, giving the five- and six-membered lactones, respectively, in fair yields; the following examples are representative. The oxidation of unsymmetrical 1,4- and 1,5-diols did not give the hydroxy ketones, but "abnormally" led to lactones (Table 1); use of AN instead of DM allows the reaction time of a diol with a long alkyl-chain to be lessened considerably without affecting the course of the reaction. This unexpected lactone formation is of special interest, because this phenomenon is markedly contrast to that observed in the conventional oxidation in aqueous medium,[2] in which secondary hydroxy group was "normally" oxidized in preference to primary one, giving the hydroxy ketone exclusively. Hence, the oxidation of various types of diols was then attempted. The oxidation of 1,2-diols gave the hydroxy ketones without concurrent

$PhCH(OH)CH_2OH \longrightarrow PhC(=O)CH_2OH$ 70%

$HOCH_2CH(OH)C_6H_{14} \longrightarrow HOCH_2C(=O)C_6H_{14}$ 76%

$HO(CH_2)_2CH(OH)Me \longrightarrow HO(CH_2)_2C(=O)Me$ 65%

Table 1. Oxidation of Unsymmetrical Diols

Diols		[1]/[Diol]	Al$_2$O$_3$	Time	Solvent	Isolated yields	
g		Mol Ratio	g	h	cm^3	%	
	(0.3)	3	1	3	DM (30)		57
		3	1	3	AN (30)		54
	(0.3)	3	3	28	DM (30)		86
		3	3	5	AN (30)		71
	(0.5)	3	3	2	DM (20)		72
	(0.3)	3	3	4	AN (30)		95
	(0.5)	3	3	3	AN (30)		71
	(0.1)	3	3	2	AN (10)		81 (by GLC)

carbon-carbon fission as shown above, while the lactones were absent. Similarly, selective formation of the hydroxy ketones from 1,3-diols was observed as typically exemplified by butane-1,3-diol (*vide supra*). On the other hand, neither a primary nor a secondary hydroxy group was selectively oxidized in the case of 1,6-diols; *viz*. hexane-1,6-diol gave a complex mixture containing the corresponding ε-lactone (Max. 38% by GLC) and heptane-1,6-diol gave both 2-methyl-ε lactone (56%) and the hydroxy ketone (44%). Thus, these diols showed the intermediate properties between those of 1,4- and 1,5-diols and 1,2- and 1,3-diols.

Although mechanistic approach is beyond this article, the varying results with the types of diols, especially the tabulated lactone formation, appears to be related to heterogeneous milieu, that is, to the stereochemistry of an adsorped diol on the alumina surface, since 1 is insoluble in DM and no perceptible reaction takes place without alumina. Accordingly, alumina plays important roles not only in increasing the active surface of a given amount of 1, but in determining reactivity of a diol and selectivity of a product.

References

1) T. Kageyama, Y. Ueno, and M. Okawara, Synthesis, **1981**, 815; M. Okawara, Yuki Gosei Kagaku Kyokai Shi, 42, 751 (1984).

2) T. Kageyama, S. Kuwahara, K. Kitahara, Y. Ueno, and M. Okawara, Chem. Lett., **1983**, 1097.

3) T. Kageyama and T. Yamamoto, Chem. Lett., **1980**, 671; *idem*. Makromol. Chem., 182, 705 (1981).

4) The present oxidation procedure using commercial dry alumina (ICN BIOMEDICALS Alumina A, Super I) is very simple and almost the same as that shown previously; M. Hirano, M. Oose, and T. Morimoto, Chem. Lett., **1991**, 331; *idem*., Bull. Chem. Soc. Jpn., **64**, 1046 (1991).