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8. This was made from commercially available Pyrex tube. One end of tube was sealed with a gas-oxygen torch and the tube was filled with phosphoric acid solution and the other end of the tube was sealed.
9. In order to determine whether saturation effects may be ignored for our pulse angle and repetition time, the same pulse angles and a pulse repetition rate of 12.7 s were applied to several samples. The change of relative peak intensities was less than 5.9% in all cases.
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11. 2.5 ppm and 5 ppm results were not included in the Table 1 and will be published.
12. After our abstract submission to the 69th Annual Meeting of the Korean Chemical Society, D. R. Gard and *et al.* (*Anal. Chem.*, **64**, 557 (1992)) published results on the application of ^{31}P-NMR for the analysis of pure sample without calibration.
13. For the 2.5 ppm sample, the signal to noise ratio was 3.7 on 37.5 h scan time in 5 mm probe of 121 MHz. In 10 mm probe at 121 MHz, about half of the time was required to get the same signal to noise ratio of 5 mm probe.

Oxidative Lactonization of Diols Using *m*-Chloroperbenzoic Acid and Hydrogen Chloride in *N,N*-Dimethylformamide

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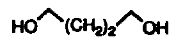
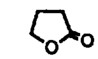
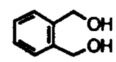
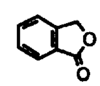
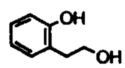
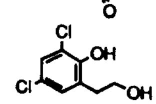
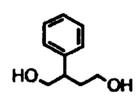
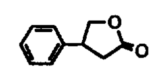
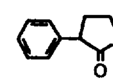
Received June 22, 1992

We have recently reported that the combination of dry HCl and *m*-chloroperbenzoic acid (MCPBA) in DMF serves as an effective reagent for the chlorination of phenols,[1] pyrimidine, purine bases and their nucleosides,[2] α-chlorination of ketones,[3] and its oxidation of secondary alcohols.[4] To our knowledge, there is no report on the application of MCPBA for lactonization of diols. In the present study, we wish to oxidative lactonization of diols using HCl/MCPBA/DMF system.

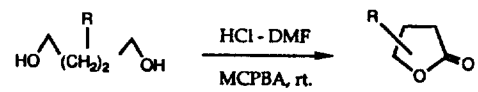
The reaction of diols **1** with dry HCl-MCPBA in DMF

Table 1. Lactonization of Various Diols Using HCl/MCPBA in DMF[5]

Entry	Diol	Reaction time	Product	Yield (%)[a]
1		0.5 h		87 (55)[b]
2		0.5 h		88 (74)[b]
3		0.5 h		65 (58)
4		0.5 h		62 (55)
				35 (30)

[a]Yields were determined by GC, and values in parentheses are isolated yield, [b]See reference 6.

at room temperature gave the corresponding lactones **2**. *m*-Chlorobenzoic acid was easily removed by washing with 5% sodium bicarbonate solution.



1 2 R= H, Phenyl

In a typical run, to a solution of 1,2-bis (hydroxymethyl)benzene (138 mg, 1.0 mmol) in 2.2 m*l* of 0.5 M HCl-DMF (1.1 mmol HCl) was a ded MCPBA (447 mg, 2.2 mmol, 85% purity) in one portion with good stirring at room temperature. The reaction mixture was allowed stirring at room temperature until yellow color disappeared. The reaction mixture was diluted with 5% aqueous $NaHCO_3$ solution and extracted with ether (3×200 m*l*). After removal of solvent *in vacuo*, the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2) to give 99 mg (74%) of γ-lactone (entry 2) as a white solid with low melting point. The lactones obtained were identified by ^{1}H NMR, IR, and mass spectra and/or comparing GC chromatograms with those of authentic samples. The representative results are summarized in Table 1.

The reaction of 1,4-butanediol with HCl-MCPBA in DMF afforded γ-butyrolactone (entry 1) in good yield but the isolated yield was comparatively low because of the difficulties in isolation. In case of symmetrical 1,2-bis(hydroxymethyl) benzene (entry 2), the best result was obtained. On the other hand, unsymmetrical diol, 2-phenyl-1,4-butandiol (entry 4) afforded a mixture of β-phenylbutyrolactone (55%) and α-phenylbutyrolactone (30%). The ratio of β-phenylbutyrolactone increased to *ca.* 70% (determined by GC) by heating (70℃) during the reaction. In case of 2-hydroxyphenethyl alcohol (entry 3), the benzene ring was chlorinated to give 3,5-dichloro-2-hydroxyphenethyl alcohol as expected.[1] The oxidation of alcohol by HCl-MCPBA in DMF seemed to be slower reaction than the chlorination to the aromatic ring. Diols which have a primary and a secondary hydroxy groups such as 2,5-pentandiol and 1-phenyl-1,4-butandiol gave the complicated results in GC analysis and we failed to isolate the desired lactones. We also examined aqueous HCl in place of dry HCl and monoperoxyphthalic acid magnesium salt (MMPP) instead of MCPBA in various solvents. The results were unsatisfactory.

In conclusion, we have found tha substituted 1,4-butandiols could be partially oxidized to lactones by enhancement of the oxidizing ability of MCPBA with HCl in DMF.

Acknowledgement. We gratefully thank the financial support from the Korea Science and Engineering Foundation.

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5. GC analysis was performed with a Helwett-Packard 5890A with a 0.2 mm×50 m fused silica capillary column, HP-1, and/or a 0.2 mm×15 m fused glycol column, HP-FFAP. Mass spectra were taken on a JEOL JMS-DX 303. Column chromatography was performed on 70-230 mesh silica gel (E. Merck).
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A New Procedure for β-Sulfenylation of α,β-Unsaturated Ketones

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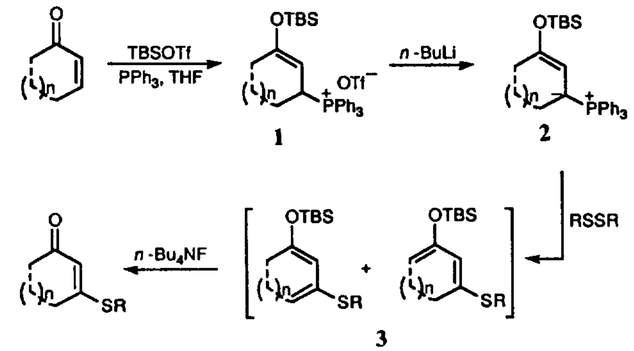
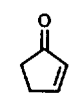
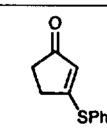
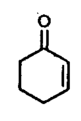
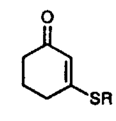
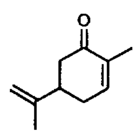
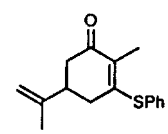
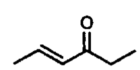
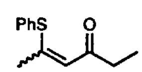
Received July 8, 1992

The generation of specific enolates *via* Michael addition of nucleophiles to α,β-unsaturated ketones has proven to be an extremely useful process for functionalization of enones.[1-5] In this regard, we have recently reported that ylides derived from enones *via* phosphoniosilylation serve effectively as β-acyl vinyl anion equivalents to give 2,3-unsaturated-1,6-dicarbonyl, β-hydroxyalkyl and 2,3-unsaturated 1,4-dicarbonyl compounds in high yields.[6] On the basis of these results, the possibility of β-sulfenylation of enones has been studied. Moreover, there are no general methods for the synthesis of β-sulfenylated α,β-unsaturated ketones, which is important in organic synthesis.[7] Also, vinyl thioethers are common synthetic intermediates being useful not only as protecting groups but also as sources of other functional groups and substituents.[8]



Scheme 1

Table 1. β-Sulfenylation of Enones

Enone	RSX	Product	Isolated yield, %[a]
	PhSSPh PhSCl		55 52
	CH_3SSCH_3 PhSSPh PhSCl		53 75 74
	PhSSPh PhSCl		74 71
	PhSSPh PhSCl		23 (1 : 1.2)[b] 65 (1 : 1.2)[b]

[a] Based on enones, [b] *cis*: *trans* ratio.

As shown in scheme 1, sulfenylation of enones at β-position was achieved by the reaction of ylides(**2**) with methyl disulfide, phenyl disulfide and benzenesulfenyl chloride followed by the elimination of triphenylphosphine with tetra-*n*-butylammonium fluoride (TBAF) to yield β-sulfenyl-α,β-unsaturated ketones in good yields. In case of acyclic enones, phenyl disulfide was used as an electrophile but gave poor results under the present conditions. Thus, the reaction of the ylide(**2**) derived from 4-hexen-3-one with phenyl disulfide gave 5-benzenesulfenyl-4-hexen-3-one in 23% yield, along with the predominant formation of several unidentified byproducts. However, the reaction of this Wittig reagent with benzenesulfenyl chloride instead of phenyl disulfide proceeded rapidly and much more cleanly, yielding 5-benzenesulfenyl-4-hexen-3-one in 65% yield. Some experimental results are given in Table 1 and illustrate the efficiency and the applicability of the present method. Especially, it is noteworthy that these overall conversions can be accomplished by one-pot procedure from α,β-unsaturated ketones without any isolation of the intermediates. The nonpolar unstable intermediates were obtained in TLC after the addition of a disulfide or benzenesulfenyl chloride. Thus, β-sulfenylation of α,β-enones may proced *via* an intermediacy of **3**. The separation and its structure determination are in progress.