

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 the substituted 1,4-butandiol could be partially oxidized to lactones by enhancement of the oxidizing ability of MCPBA with HCl in DMF.

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A New Procedure for β -Sulfenylation of α,β -Unsaturated Ketones

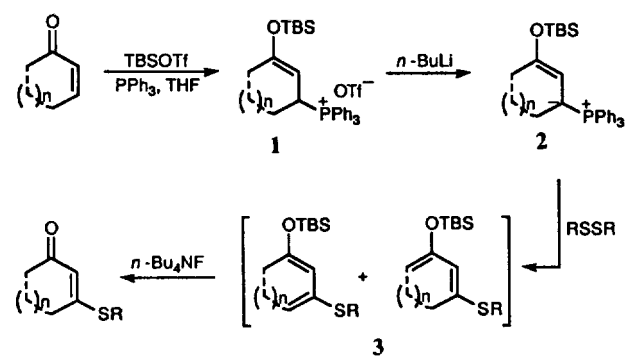
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The generation of specific enolates *via* Michael addition of nucleophiles to α,β -unsaturated ketones has proven to be an extremely useful process for functionalization of enones.¹⁻⁵ In this regard, we have recently reported that ylides derived from enones *via* phosphonosilylation 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	R SX	Product	Isolated yield, % ^a
	PhSSPh		55
	PhSCl		52
	CH ₃ SSCH ₃		53
	PhSSPh		75
	PhSSPh		74
	PhSCl		71
	PhSSPh		23 (1:1.2) ^b
	PhSCl		65 (1:1.2) ^b

^aBased on enones, ^bcis: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 benzenesulfonyl 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-benzenesulfonyl-4-hexen-3-one in 23% yield, along with the predominant formation of several unidentified byproducts. However, the reaction of this Wittig reagent with benzenesulfonyl chloride instead of phenyl disulfide proceeded rapidly and much more cleanly, yielding 5-benzenesulfonyl-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 benzenesulfonyl chloride. Thus, β -sulfenylation of α,β -enones may proceed *via* an intermediacy of 3. The separation and its structure determination are in progress.

The typical procedure for β -benzenesulfonylation of enones is as follows. To a solution of triphenylphosphine (252.4 mg, 0.97 mmol) in tetrahydrofuran (4 ml) were added 2-cyclohexen-1-one (88.4 mg, 0.92 mmol) and TBSOTf (266.9 mg, 1.01 mmol) at 0°C. After being stirred at room temperature for 30 min, the reaction mixture was cooled to -78°C and *n*-butyllithium (0.58 ml, 0.97 mmol) was added dropwise to give a black-colored solution. The reaction mixture was stirred for 30 min at -78°C and phenyl disulfide (220.5 mg, 1.01 mmol) in tetrahydrofuran (3 ml) was added to the ylide solution. After being warmed to room temperature, TBAF (1.38 ml, 1.38 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. The extractive work-up and chromatographic separation gave 3-benzenesulfonyl-2-cyclohexen-1-one (140.8 mg, 75%).

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Preparation of Lithium Dialkylaminoaluminum Hydrides. A New Class of Reducing Agents

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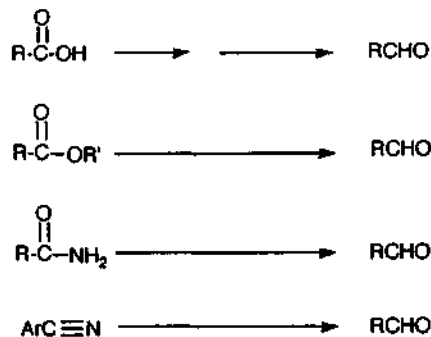
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The reaction in tetrahydrofuran of lithium aluminum hy-

dride with representative dialkylamines of varying steric requirements was examined in detail to establish the generality of this synthesis of the corresponding lithium dialkylaminoaluminum hydrides, $\text{Li}(\text{R}_2\text{N})_n\text{AlH}_{4-n}$, ($n=2, 3$). In cases involving a less hindered dialkylamine, such as diethylamine, di-*n*-butylamine and di-*n*-hexyl amine, the reaction is very fast and gives the corresponding trisubstituted derivatives cleanly. However, a moderately hindered dialkylamine, such as diisobutylamine, reacts with lithium aluminum hydride slowly to afford the corresponding disubstituted derivative at 25°C. In this case a trisubstituted derivative can also be obtained under reflux. The reaction of more hindered dialkylamine, such as diisopropylamine and dicyclohexylamine, is sluggish even at 50°C and gives the corresponding disubstituted derivatives cleanly. Cyclic secondary amines, such as pyrrolidine, piperidine, morpholine and *N*-methylpiperazine, undergo the reaction rapidly to yield the corresponding trisubstituted derivatives even at 0°C. Finally, the reaction with diphenylamine gives the corresponding disubstituted derivative cleanly.

Trisubstituted aluminohydrides, such as lithium trimethoxy-, triethoxy- and tri-*t*-butoxyaluminohydrides, have evolved as attractive selective reducing agents in organic synthesis.¹ They have been synthesized by treatment of 1 equiv of lithium aluminum hydride solution with 3 equiv of the corresponding alcohols.^{1d,2}

Recently we synthesized some dialkylamino-substituted derivatives of lithium aluminum hydride and applied them to the selective reduction of organic functionalities. They have proven to be useful selective reducing agents, especially in the conversion of carboxylic acid derivatives into the corresponding aldehydes.³ These unique characteristics have been of great interest. Accordingly, we undertook a study to develop a general procedure for the synthesis of lithium dialkylaminoaluminum hydrides in tetrahydrofuran with various dialkylamines of different steric environments.



Results and Discussion

A representative series of dialkylamines with various steric and electronic environments were selected for the present study and their reaction with lithium aluminum hydride studied. The stability of the resulting lithium dialkylaminoaluminum hydrides was also examined by ²⁷Al-NMR spectra and measuring the number of moles of H₂ evolved by hydrolysis of aliquots of the reagent solution at appropriate time intervals. The reagent were characterized by IR and ²⁷Al-NMR spectroscopy.

The approximate rates and stoichiometry of the reaction