

show the isosbestic point at 308 nm indicating that TMP is converted into the complex. TMP carbonyl stretching vibration at 1705cm^{-1} is little shifted but a new broad band appeared at $1040\text{--}1110\text{cm}^{-1}$ suggesting that carbonyl oxygen of TMP does not strongly interact with BF_3 . Figure 4 shows the fluorescence spectra of TMP in the absence and presence of $\text{BF}_3\cdot\text{OEt}_2$ at room temperature. The large Stokes shifts [$\Delta\lambda = \lambda_{\text{max}}^f$ (the fluorescence maximum) $-\lambda_{\text{max}}$ (the absorption maximum)] are observed as the concentration of $\text{BF}_3\cdot\text{OEt}_2$ is increased. The position of λ_{max}^f (425 nm) is considerably shifted towards the longer wavelength (475 nm) and the fluorescence intensity is gradually increased.

The results, which are reminiscent of the behavior of simpler carbonyls, can be interpreted in terms of the energy level disposition of the $^3(n, \pi^*)$ state relative to the lowest energy $^1(\pi, \pi^*)$ state.⁹ In TMP, the $^3(n, \pi^*)$ state lies below $^1(\pi, \pi^*)$ state and the $^1(\pi, \pi^*) \rightarrow ^3(n, \pi^*)$ intersystem crossing is efficient due to relatively strong $(n, \pi^*)\text{--}(\pi, \pi^*)$ spin-orbit coupling. In the complex, coordination of the nonbonding electrons of the α, β -unsaturated carbonyl group results in lowering the $^1(\pi, \pi^*)$ energy level as well as the redistribution of the orbital electron densities and the $^3(n, \pi^*)$ state becomes higher than the $^1(\pi, \pi^*)$ state.¹⁰ The energy level ordering is reversed so that the fluorescence becomes competitive with intersystem crossing. Kearns *et al.* expected $^1(\pi, \pi^*) \rightarrow ^3(n, \pi^*)$ transition to be $10^2\text{--}10^3$ times more efficient than $^1(\pi, \pi^*) \rightarrow ^1(\pi, \pi^*)$ transitions.¹¹

Unlike the BF_3 -catalyzed photodimerization of coumarin and cinnamic esters in which the reactivity and stereoselectivity are enhanced, an unusual Lewis acid effect was observed in the photodimerization of TMP. Increasing $\text{BF}_3\cdot\text{OEt}_2$ concentration decreases the quantum yield of dimerization. The kinetics and mechanism of the BF_3 -catalyzed reaction

are currently under investigation to elucidate the reactive species and exact reason of the abnormal effect. The complexation, however, should substantially change both the ground and excited-state energies and the energy level ordering and thus account for the reactivity change observed in the presence of $\text{BF}_3\cdot\text{OEt}_2$.

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A Novel Method for Conversion of Lactones into ω -Bromoalkyl Sulfides

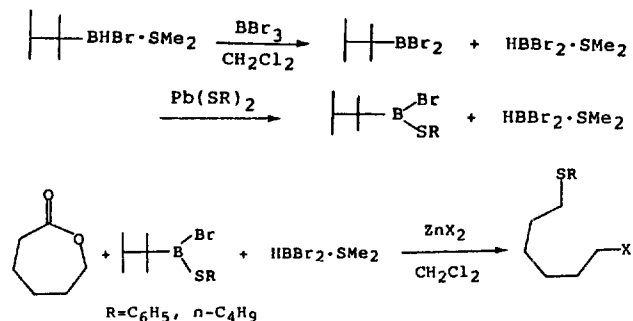
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





We have previously reported a novel method for direct conversion of carboxylic acids and carboxylic esters into *S,S'*-diphenyl acetals and phenyl sulfides with thexylphenylthioborane.^{1,2} During the course of mechanistic studies, it has been found that lactones can be converted into ω -haloalkyl phenyl sulfides with phenyl thexylbromothioborinate and dibromoborane-dimethyl sulfide in the presence of zinc halide. As far as we are aware, this is the first example in which carbonyl and alkoxy group are simultaneously transformed to the sulfide and the halo group, respectively, by an one-pot procedure.

An equimolar mixture of phenyl thexylbromothioborinate and dibromoborane-dimethyl sulfide was prepared by the



reaction of thexylbromoborane-dimethyl sulfide with boron tribromide in dichloromethane followed by treatment with

Table 1. Direct Conversion of Lactones into ω -Haloalkyl Sulfides^a

lactone	method ^b	product	yield, % ^c
	A	C ₆ H ₅ SCH ₂ (CH ₂) ₄ CH ₂ Br	72
	B	n-C ₄ H ₉ SCH ₂ (CH ₂) ₄ CH ₂ Br	68
	A ^d	C ₆ H ₅ SCH ₂ (CH ₂) ₄ CH ₂ I	71(7)
	B ^d	n-C ₄ H ₉ SCH ₂ (CH ₂) ₄ CH ₂ I	59(15)
	A	C ₆ H ₅ SCH ₂ CH(CH ₂) ₃ CH ₂ Br	65
	B	n-C ₄ H ₉ SCH ₂ CH(CH ₂) ₃ CH ₂ Br	67
	A ^d	C ₆ H ₅ SCH ₂ CH(CH ₂) ₃ CH ₂ I	62(8)
	A	C ₆ H ₅ SCH ₂ (CH ₂) ₄ CHBrCH ₃	64
	B	n-C ₄ H ₉ SCH ₂ (CH ₂) ₄ CHBrCH ₃	68
	A	C ₆ H ₅ SCH ₂ (CH ₂) ₅ CH ₂ Br	69
	B	n-C ₄ H ₉ SCH ₂ (CH ₂) ₅ CH ₂ Br	52
	A	C ₆ H ₅ SCH ₂ (CH ₂) ₁₀ CH ₂ Br	63
	B	n-C ₄ H ₉ SCH ₂ (CH ₂) ₁₀ CH ₂ Br	67
	A	C ₆ H ₅ SCH ₂ (CH ₂) ₁₀ CH ₂ Br	81
	B	n-C ₄ H ₉ SCH ₂ (CH ₂) ₁₀ CH ₂ Br	83

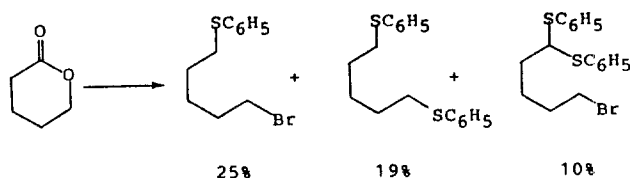
^aThe reaction was carried out with 3.0 equiv of the reagent in the presence of 1.0 equiv of zinc bromide in dichloromethane at room temperature for 24 h. ^bMethod A: phenyl hexylbromothioborinate/dibromoborane-dimethyl sulfide. Method B: n-butyl hexylbromothioborinate/dibromoborane-dimethyl sulfide. ^cIsolated yields of ω -haloalkyl sulfides. The numbers in parenthesis indicate the yield of the corresponding bromides. ^d1.0 Equiv of zinc iodide was used.

0.5 equiv of bis(phenylthio) lead.³ The reagent in dichloromethane can be stored in a refrigerator for several weeks without little decomposition. An equimolar mixture of n-butyl hexylbromothioborinate and dibromoborane-dimethyl sulfide was prepared in a similar manner using bis(n-butylthio) lead.

After much experimentation to find out an optimum condition, it was found that the reaction of ϵ -caprolactone with 3.0 equiv of an equimolar mixture of phenyl hexylbromothioborinate and dibromoborane-dimethyl sulfide in the presence of 1.0 equiv of zinc iodide in dichloromethane at room temperature for 18 h gave 6-iodohexyl phenyl sulfide in 71% yield together with a small amount of 6-bromohexyl phenyl sulfide. The use of zinc bromide gave exclusively 6-bromohexyl phenyl sulfide in 72% yield under the similar conditions. 2-Methyl ϵ -caprolactone was converted into 6-bromo-2-methylhexyl phenyl sulfide in 65% yield, indicating nucleophilic cleavage of the alkyl-oxygen bond by bromide anion. The ring opening of lactones by the nucleophilic cleavage of

the alkyl-oxygen bond has been previously reported. The examples include iodotrimethylsilane,⁴ sodium phenyl selenolate,⁵ aluminum halide/thiol,⁶ and boron tribromide⁷ which allow the conversion of lactones into synthetically useful ω -functionalized carboxylic acids.

Table 1 includes some experimental results and illustrates the applicability, efficiency, and the scope of the method. The present method works well with 8-membered and macrocyclic lactones. However, this method reaches a limit with γ - and δ -lactone. For instance, δ -valerolactone produced 5-bromopentyl phenyl sulfide in 25% yield along with several byproducts. The similar result was obtained with γ -butyrolactone.



The reaction was also carried out with an equimolar mixture of n-butyl hexylbromothioborinate and dibromoborane-dimethyl sulfide. The reaction proceeded smoothly, yielding ω -bromoalkyl n-butyl sulfides. The scope and limitations were almost identical with phenyl hexylbromothioborinate and the results are summarized in Table 1.

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- To a solution of hexylbromoborane-dimethyl sulfide (5.93 g, 25 mmol) in dichloromethane (80 ml) under nitrogen at room temperature was added boron tribromide (6.25 g, 25 mmol). The reaction mixture was stirred for 1 h, followed by the addition of bis(phenylthio) lead (5.3 g, 12.5 mmol). After being stirred for 0.5 h, precipitated lead bromide was removed and the concentration of the reagent was adjusted to 0.25 M solution by adding dichloromethane.
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