

For the chiral induction experiment, (*R*)-(+)-1,1'-bi-2-naphthol was used to prepare the optically active monofarnesate ester (*R*)-5. Cyclization of (*R*)-5 and the reduction of the resultant (*R*)-6 with lithium aluminum hydride yielded optically active drimenol (-)-7. ($[\alpha]_D^{27} = -5.4^\circ$, $c = 0.41$, benzene; literature value,⁹ $[\alpha]_D^{27} = -19.1^\circ$, $c = 0.76$, benzene) Analysis of the high resolution nmr spectrum¹⁰ of the ester 9 prepared from (-)-7 and (*R*)-MTPA chloride led to a more dependable optical purity value (20% *e.e.*) of the product. (Scheme 4)

In conclusion, use of optically active 1,1'-bi-2-naphthol as a chiral auxiliary in the acid catalyzed cyclization of monocyclofarnesate resulted in a moderately low chiral induction. Employment of other chiral agents for more efficient asymmetric synthesis of this important class of compounds will be the subject of future studies.

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5. A small amount of (*Z*)-binaphthyl ester was also formed in the esterification step, which was removed via silica gel column chromatography.
6. The structure of the acetate 8 was confirmed by extensive spectroscopic analysis including attached proton test and ¹³C-¹H chemical shift correlation spectrum: ¹H nmr (CDCl₃, 360 MHz) δ 0.81(s, 3H), 0.86(s, 3H), 0.88(s, 3H), 1.05-1.25(m, 5H), 1.45(m, 2H), 1.66(s, 3H), 1.90-2.05(m, 3H), 2.03(s, 3H), 4.07(dd, $J = 12$ and 6 Hz, 1H), 4.24(dd, $J = 12$ and 3 Hz, 1H), 5.49(m, 1H); ¹³C nmr (CDCl₃, 360 MHz) δ 14.43(C-13), 18.69(C-2), 21.20(C-17), 21.66(C-15), 21.89(C-12), 23.57(C-6), 32.92(C-4), 33.26(C-11), 35.92(C-10), 39.52(C-1), 42.06(C-3), 49.83(C-5), 53.35(C-9), 63.15(C-14), 123.63(C-7), 132.44(C-8), 171.08(C-16). See also: "Interpretation of Carbon-13 NMR Spectra", F. W. Wehrli; T. Wirthlin.; Heyden: London, p. 44 (1978)
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10. In the ¹H nmr spectrum (CDCl₃, 360 MHz) of the MTPA ester 9, protons on C-13 and C-14 exhibited split signals in addition to the split signals for the methoxy protons of the MTPA moiety. These were used in the determination of optical purity of the sample. Note that (*S*)-(-)-MTPA acid is converted to (*R*)-MTPA chloride, which is used for the synthesis of (*S*)-MTPA esters.

Unusual "Lewis Acid" Effect on the Photodimerization of 4,5',8-Trimethylpsoralen(TMP)

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Many reactions of α,β -unsaturated carbonyl and nitrile compounds are catalyzed by Lewis acids. These include, for example, catalyzed Diels-Alder reactions, alternating copolymerizations, [2 + 2] cycloadditions, aldol condensations, and several photoreactions. Especially in Diels-Alder and ene reactions, the enhanced reactivity and stereoselectivity have been attributed to changes in frontier orbital energies and C=C double bond polarity upon complexation of the carbonyl oxygen.¹ Lewis *et al.* have reported that Lewis acid complexation of α,β -unsaturated esters results in marked changes in their spectroscopic properties and unimolecular photochemistry.² The possibility that Lewis acids might also serve as catalysts for bimolecular photochemical reactions is suggested by reports concerning the photodimerization

of dibenzylideneacetone in the presence of SnCl₄³, by preliminary reports concerning the effect of Lewis acids on the photodimerization of coumarin^{4(a)} and cinnamic esters,^{4(b)} and by a recent report of selective head-to-head dimerization of cyclopentenone in the presence of SnCl₄⁵.

We have initiated a study on the photodimerization of a biologically important furocoumarins in the presence of Lewis acids. Because of the importance of psoralens(furocoumarins) in the treatment of psoriasis and vitiligo, the photophysical properties of the lowest excited states(singlet and triplet) of furocoumarins and coumarins have been extensively investigated in recent years.⁶ The excited states of 4,5',8-trimethylpsoralen(TMP) have been investigated in rigid matrices at 12 and 77K by means of luminescence and

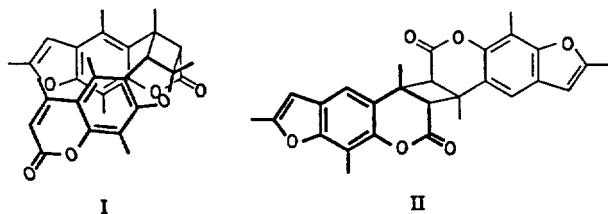


Figure 1. Stereochemical structure of photoproduct: pyrone<>furan, cis-syn dimer(I) and pyrone<>pyrone, trans-anti dimer(II).

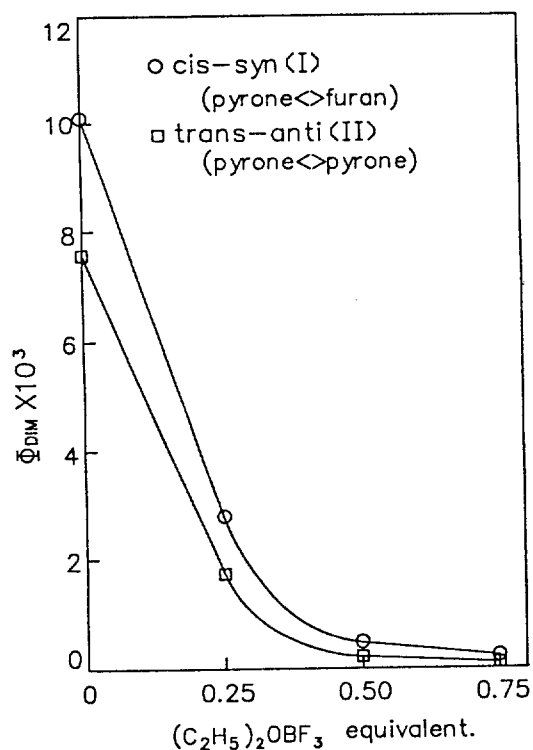


Figure 2. Quantum yields for photodimerization of 3×10^{-2} M TMP solution.

photoselection measurements.⁷ These studies indicate that the lowest singlet excited state of TMP is a (π, π^*) state but considerably below the second $^1(\pi, \pi^*)$ state and $^3(n, \pi^*)$ state is located slightly below the lowest $^1(\pi, \pi^*)$ state.

The photodimerization of TMP in dichloromethane solution has been investigated.⁸ The pyrone<>furan, cis-syn dimer(I) and the pyrone<>pyrone, trans-anti dimer(II) are the major ($\Phi = 1.0 \times 10^{-2}$ for 3×10^{-2} M TMP) and minor ($\Phi = 7.6 \times 10^{-3}$ for 3×10^{-2} M TMP) photoproducts, respectively (Figure 1). The stereochemical structures of photoproducts were assigned by a shift reagent(EuFOD) and NOE experiments. The results show that the dimerization from the stacked species is more efficient than that from the non-stacked species. The effect of $\text{BF}_3 \cdot \text{OEt}_2$ concentration on the quantum yield for photodimerization of 3.0×10^{-2} M TMP is shown in Figure 2. Increasing concentration of $\text{BF}_3 \cdot \text{OEt}_2$ leads to a decrease of quantum yield which is exactly opposite compared to the BF_3 -catalyzed photodimerization of coumarin.

The UV absorption spectra of TMP in the absence and presence of $\text{BF}_3 \cdot \text{OEt}_2$ are shown in Figure 3. As the concen-

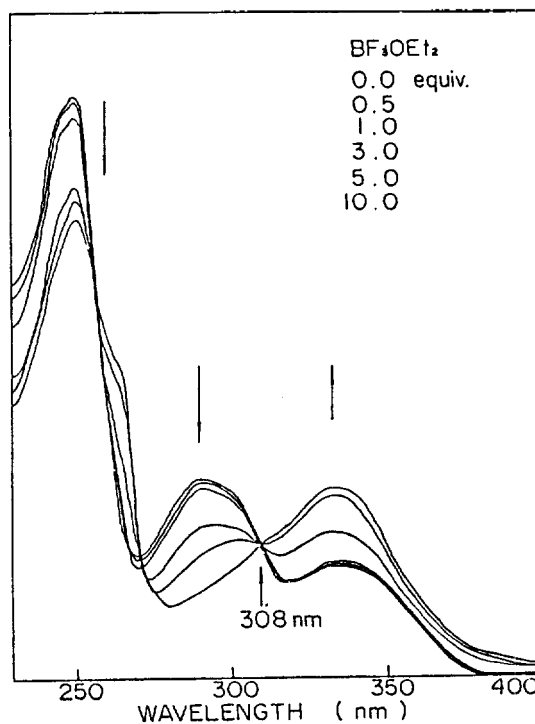


Figure 3. UV absorption spectra of TMP in the absence and presence of Lewis acids.

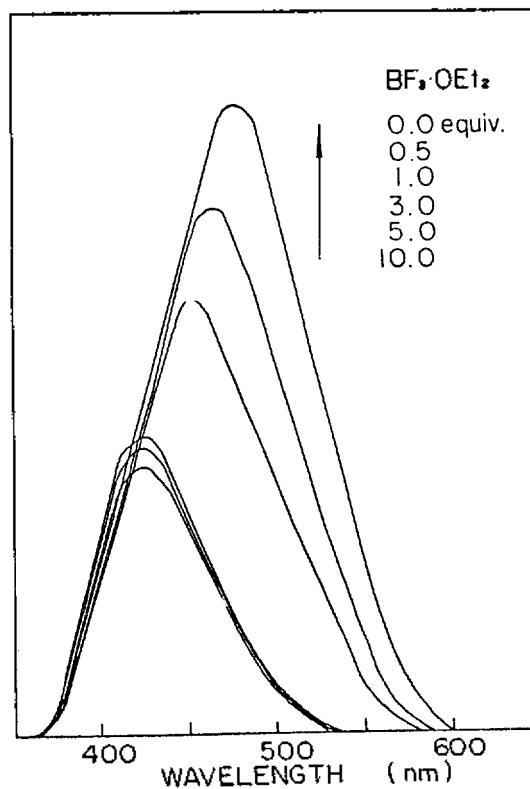


Figure 4. Fluorescence emission spectra of TMP in the absence and presence of Lewis acid.

tration of $\text{BF}_3 \cdot \text{OEt}_2$ increased, the intensity of 335 nm band increased and that of 290 nm and 250 nm bands decreased and a shoulder appeared at 265 nm. The absorption spectra

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 [$\Delta\lambda = \lambda'_{\text{max}} - \lambda_{\text{max}}$ (the fluorescence maximum) - λ_{max} (the absorption maximum)] are observed as the concentration of $\text{BF}_3\cdot\text{OEt}_2$ is increased. The position of λ'_{max} (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

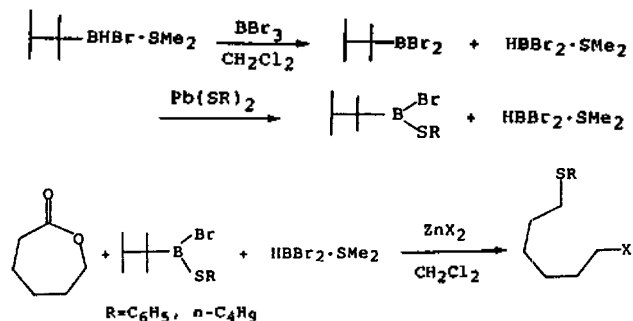
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We have previously reported a novel method for direct conversion of carboxylic acids and carboxylic esters into *S,S'*-diphenyl acetals and phenyl sulfides with thexylphenylthioborane.^{1,2} During the course of mechanistic studies, it has been found 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