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17. Prof. Neier reports<sup>6</sup> that 5-cyanovalulinic acid is a good inhibitor ( $K_i/K_m=0.19$ ) of the *Rhodospseudomonas spheroides* enzyme. He explained this result by the preferred formation of the enamine in the "wrong" position of carbon 4 and 5 instead of 3 and 4 at the active-site of the enzyme. 5-Fluorovalulinic acid may act in the same way with bovine liver enzyme as 5-cyanovalulinic acid with the *R. spheroides* enzyme. However, the question is still open that  $K_i/K_m$  value of 5-fluorovalulinic acid is much smaller than that of 5-cyanovalulinic acid while tendency for 5-cyanovalulinic acid to make the enamine in the "wrong" position is much greater.
18. Further efforts are in progress to find out the correlation between binding and the electronic environment by the calculation of the atomic charges of the substrate and its analogues using MOPAC.

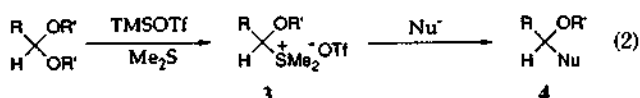
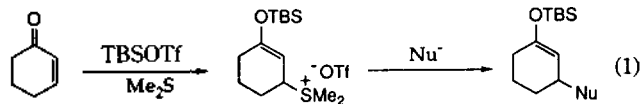
### Facile Nucleophilic Substitution of $\alpha$ -Alkoxy-sulfonium Salts

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Sulfonium salts have been mainly utilized in the preparation of sulfur ylides<sup>1</sup> and the synthetic application of sulfonium salts as leaving groups has been limited due to their relatively poor leaving group ability.<sup>2</sup> During the study of selective protection of ketones in the presence of aldehydes,<sup>3</sup> we have experienced the unusually high reactivity of  $\alpha$ -silyloxysulfonium salts toward several nucleophiles. Furthermore, we have reported that 3-trialkylsilyloxy-2-alkenylene-sulfonium salts, derived from sulfoniosilylation of  $\alpha,\beta$ -enones, are highly reactive species and undergo facile nucleophilic substitution reactions to give the products bearing the silyl enol ether group (Eq. 1).<sup>4</sup> In this paper we wish to report (i) the formation of  $\alpha$ -alkoxy-sulfonium salts from acetals and (ii) their reactivity toward nucleophiles (Eq. 2).



1: R=n-C<sub>3</sub>H<sub>7</sub>; R'=Me  
2: R=n-C<sub>8</sub>H<sub>17</sub>; R'=Et

Reaction of 1 with trimethylsilyl triflate (TMSOTf, 1.1 equiv) and dimethyl sulfide (1.2 equiv) in tetrahydrofuran,

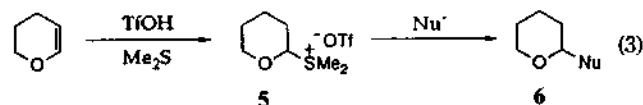
**Table 1.** Nucleophilic Substitution of  $\alpha$ -Alkoxy-sulfonium Salt (3) with Nucleophiles

Nucleophile <sup>a</sup>	Temp, °C	Time, h	Product	Yield, % <sup>b</sup>
RMgBr <sup>c</sup>				
R = Me	-78	3	R = Me	82
= Ph	-78	1	= Ph	95
= C≡C-Ph	-78→0	1	= C≡C-Ph	77
= CH=CH <sub>2</sub> <sup>d</sup>	-78	2	= CH=CH <sub>2</sub>	95
	-30	5	= CH <sub>2</sub> CH=CH <sub>2</sub>	96
	-78	1	= CH <sub>2</sub> CH=CH <sub>2</sub>	95
PhS-SiMe <sub>3</sub>	-78	3	= SPh	82
PhSLi <sup>e</sup>	-78	1	= SPh	91
	-30	1		73
	-30	3		82

<sup>a</sup>1.2 equiv of the nucleophile was used. <sup>b</sup>The yield refers to the isolated yield. <sup>c</sup>A tetrahydrofuran solution of nucleophiles was added. <sup>d</sup>0.1 equiv of CuBr-SMe<sub>2</sub> was added.

ether, or dichloromethane at -78°C afforded 3, which was characterized by the low temperature <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> at -40°C.<sup>5</sup> The reaction proceeded cleanly and almost instantly. Simple dialkyl sulfide and tetrahydrothiophene could be successfully employed but diphenyl sulfide failed to form the corresponding sulfonium salts due to its low nucleophilicity. The sulfonium salts were thermally unstable and decomposed above -20°C. Furthermore, it is noteworthy that the present reaction did not work with the ketals due to steric reasons.

Nucleophilic substitution reactions of  $\alpha$ -alkoxy-sulfonium salts (3) were generally carried out in dichloromethane using several nucleophiles by one-pot procedure as shown in Table 1. Reaction of 3 in dichloromethane with tetrahydrofuran solution of methylmagnesium bromide proceeded cleanly at -78°C, yielding the desired product in high yield. The use of phenylethynylmagnesium bromide required higher temperature and vinylmagnesium bromide failed to react with 3. However, in the presence of 0.1 equiv of cuprous bromide, the reaction occurred smoothly. 3 was also reactive toward allyltrimethylsilane, silyl enol ethers, and phenylthiotrimethylsilane. Among three different types of silyl related functional groups, phenylthiotrimethylsilane was the most reactive, yielding the synthetically useful O,S-acetals<sup>6</sup> which could be also prepared by treatment of 3 with lithium thiophenoxide.



Nu<sup>-</sup>: PhMgBr (91%); Ph-C(OTMS)=CH<sub>2</sub> (70%); PhSTMS (85%)

In order to study the possibility of extending the present

method to carbohydrates, we examined the nucleophilic substitution of **5** with several nucleophiles under the similar conditions (Eq. 3). **5** was generated by treatment of 3,4-dihydro-2H-pyran with 1.0 equiv of triflic acid in the presence of 1.5 equiv of dimethyl sulfide at  $-78^{\circ}\text{C}$  in dichloromethane. **5** worked well with Grignard reagents, silyl enol ethers and phenylthiotrimethylsilane but failed to react with allyltrimethylsilane.

In conclusion, we have shown that previously unknown  $\alpha$ -alkoxysulfonium salts are very reactive species and undergo facile nucleophilic substitution reactions with a variety of nucleophiles under mild conditions.

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5. **3** ( $R=n\text{-C}_3\text{H}_7$ ,  $R'=\text{Me}$ ):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $-40^{\circ}\text{C}$ )  $\delta$  0.20 (s, 9H), 0.90-1.00 (b, s, 3H), 1.40-1.65 (m, 2H), 1.65-1.90 (m, 2H), 2.70 (s, 3H), 2.85 (s, 3H), 3.60 (s, 3H), 5.41 (b, s, 1H).
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### Synthesis and Properties of Photosensitive Polyimides Containing Cyclobutane Ring Structure

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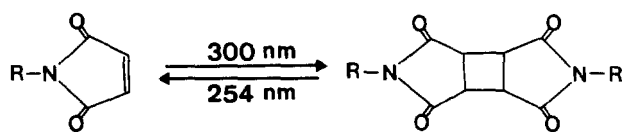
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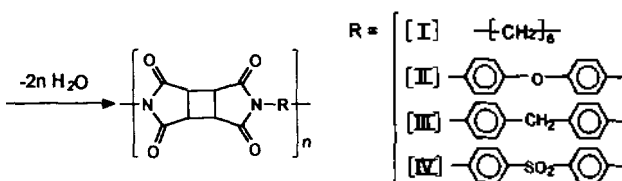
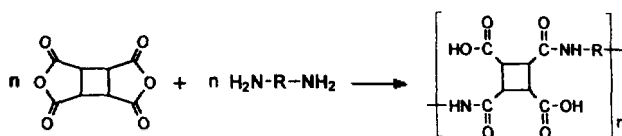
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Polyimides are well known not only for their chemical and thermal stabilities but also for their excellent electrical and mechanical properties. They are used as encapsulants, insulators and flexible substrates for printed circuits in the



Scheme 1.



Scheme 2.

electronics industry. Recently, the use of polyimides as polymer materials for electronic applications has become increasingly important because it not only has many excellent properties but also simplifies the VLSI fabrication processes.<sup>1-3</sup> For these purposes, solvent soluble<sup>4-5</sup> and/or photosensitive polyimides<sup>6-10</sup> have been developed.

Irradiation of maleimide derivatives with 300 nm UV light produces cyclobutane photodimers,<sup>11</sup> and photolysis of these photodimers with 254 nm UV light results in original maleimide derivatives by the cycloreversion process as shown in Scheme 1. In continuation of our studies on the application of photochemical reactions to the polymer systems,<sup>12</sup> the present communication reports a synthesis and properties of photosensitive polyimides containing cyclobutane ring in the main chain. This type of polyimides may be used as a promising positive deep UV photoresist that can be developable in organic solvents.<sup>13</sup>

The synthetic method of polyimides containing cyclobutane ring is shown in Scheme 2. Maleic anhydride cyclobutane dimer was obtained by irradiation of maleic anhydride with 300 nm UV light in  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$ .<sup>11</sup> Polyamic acid [I]-[IV] was synthesized by the reaction of maleic anhydride cyclodimer (5 mmol) with corresponding diamine (5 mmol) in 20 ml dimethylacetamide (DMAc) at room temperature. The polyamic acid was purified by precipitation of the reaction mixture in MeOH. The polyimide was obtained by heating the polyamic acid stepwise at  $150^{\circ}\text{C}$  for 5 hrs,  $200^{\circ}\text{C}$  for 5 hrs,  $250^{\circ}\text{C}$  for 2 hrs, and  $300^{\circ}\text{C}$  for 2 hrs.

Physical properties of the polyamic acid and polyimide are summarized in Table 1. The precursor of the polyimide, polyamic acid was soluble in polar aprotic solvents such as DMAc or N-methyl-2-pyrrolidinone (NMP) and inherent viscosity of the polyamic acid measured in DMAc solution ranged between 0.5-0.9 dl/g indicating relatively high molecular weights. DSC analysis shows that the decomposition of poly-