## CONVERSION OF LACTONE INTO LACTONE HEMITHIOACETAL AND SYNTHESIS OF ENOL LACTONE

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Lactone hemithioacetal was synthesized in good yield from  $\omega$ -phenylthiocarboxylic acid derived from lactone, and it was converted into enol lactone via the corresponding sulfoxide.

The introduction of functional groups into the  $\alpha$ -methylene group of lactone has been well established, because of the easy formation of its enolate anion. We now wish to report phenyl-sulfenylation at the  $\omega$ -methylene group in lactone followed by the conversion of the product 3 into enol lactone 4 as shown in Scheme.



Scheme

Five- or six-membered lactone was transformed into the corresponding  $\omega$ -phenylthiocarboxylic acid 2 in acceptable yield by treatment with benzenethiol and Lewis acid (AlBr<sub>3</sub>, BBr<sub>3</sub>, or tri-n-butyltin triflate). The reaction required longer time and higher temperature compared to that with alkanethiol and Lewis acid,<sup>1</sup> because of lower nucleophilicity of benzenethiol than that of alkanethiol.

Successive conversion of the acid 2 into lactone hemithioacetal 3 was easily achieved by intramolecular cyclization reaction; the acid 2 on treatment with N-chlorosuccinimide in toluene or carbon tetrachloride under nitrogen afforded  $\frac{3}{3}$  in good yield.<sup>2,3</sup> The results were summarized in Table. The stereoisomers of  $\frac{3}{20}$  obtained from acid  $\frac{2}{20}$  were easily separated by preparative TLC in a 1:1 ratio.<sup>4</sup>

Oxidation of 3b and 3e with MCPBA followed by elimination by heating the resulting sulfoxide



						the second			
ring opening of lactone $l_{\lambda}^{a}$						Pummerer type reaction of $2^{b}_{\sim}$			
1		Lewis acid	(yield	%) <sup>C</sup> 2 ~		reaction time (h)	(yield 🖇	%) <sup>c</sup> 3 <sup>c</sup>	
°	la ~~	(n-Bu)₃SnOTf <sup>d</sup>	(54)	CO <sub>2</sub> H SC <sub>6</sub> H <sub>5</sub>	2a ~~	0.5	(83)		3a ~~
C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> 0	1b ~~	BBr <sub>3</sub>	(69)	C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H SC <sub>6</sub> H	2b ~~	1	(85)		3b ~~
	1c ~~	AlBr <sub>3</sub>	(49)	SC 6 H	2c ~~	1	(86)		3c ~~
	1d ~~	AlBr <sub>3</sub>	(31)		2d ~~	0.5 <sup>e</sup>	(55)	C SC <sup>e</sup> H <sup>2</sup>	3d ~~
X	0 ) <u>le</u>	A1Br₃	(49)	CO2H SC6H	2e ~~	2 <sup>f</sup>	(65)		3e ~~
le		BBr₃	(49)	2e					

Table Conversion of lactone 1 to lactone hemithioacetal 3 via  $\omega$ -phenylthiocarboxylic acid 2

a) Reaction was carried out in benzenethiol unless otherwise noted. b) Acid 2 was treated with one molar equivalent of NCS in toluene at ambient temperature under nitrogen unless otherwise noted. c) Isolated yield. d) Co-solvent: dichloromethane. e) Reaction solvent: a l:l mixture of dichloromethane and carbon tetrachloride. f) Reaction solvent: carbon tetrachloride.

gave rise to enol lactones 4b and 4e in 70% and 63% yield, respectively. As expected, the sulfoxide derived from  $3c_{\alpha}(\alpha-SC_{6}H_{5})$  showed no change on prolonged heating in carbon tetrachloride. However another sulfoxide obtained from  $3c_{\alpha}(\beta-SC_{6}H_{5})$  produced an unstable enol lactone 4c which was isomerized to  $\alpha\beta$ -unsaturated lactone  $5^{5}$  during isolation by preparative TLC (62% yield).

## References and Notes

- 1) M. Node, K. Nishide, M. Sai, and E. Fujita, Tetrahedron Lett., 1978, 5211.
- 2) C. G. Kruse, E. K. Poels, F. L. Jonkers, and A. van der Gen, J. Org. Chem., 43, 3548 (1978).
- The addition of triethylamine in order to scavenge hydrogen chloride produced during the reaction gave somewhat lower yield of 3.
- 4) 3c;  $\alpha$ -SC<sub>6</sub>H<sub>5</sub>: NMR  $\delta$  5.63 ppm (1H, d, J = 3.9 Hz,  $\geq$ C<u>H</u>-SC<sub>6</sub>H<sub>5</sub>);  $\beta$ -SC<sub>6</sub>H<sub>5</sub>: NMR  $\delta$  5.44 ppm (1H, d,  $J = 2.2 \text{ Hz}, \geq$ C<u>H</u>-SC<sub>6</sub>H<sub>5</sub>).
- 5) D. Butina and F. Sondheimer, Synthesis, 1980, 543.

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