## Thionolactone Claisen Rearrangement

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Thionolactones prepared from the corresponding  $\gamma$ -lactones are found to be good substrates for the Claisen rearrangement.

Synthetic utility of thionolactones has not been fully explored to date. We report here the first example of a synthetically promising Claisen type rearrangement using  $\gamma$ -thionolactone substrates, <u>1</u> and <u>2</u>, prepared from the lactone precursors<sup>1</sup>) with Lawesson reagent.<sup>2-4</sup>) The reaction allows introduction of an allylic substituent on the  $\alpha$ -position of the substrates under mild conditions. The reaction may be reiteratively carried out to afford  $\alpha, \alpha$ -bis-allylated products. Although the reaction proceeds non-stereoselectively in the first rearrangement generating tertiary center probably due to facile epimerization under the conditions, the second rearrangement takes place predominantly from the less crowded <u>anti</u> face to the  $\gamma$ -substituent.<sup>9</sup> In contrast to thio-amides<sup>5,6</sup> and thio-lactams<sup>6-8</sup> the thionolactones are inert to allyl halides without catalyst and therefore activation by potassium <u>t</u>-butoxide is unavoidable to generate a ketene thioacetal intermediate.<sup>10</sup>



A typical procedure is as follows; To a stirred solution of the thionolactone (1, 440 mg, 20 mmol) in THF (12 ml) is added potassium <u>t</u>-butoxide (269 mg, 2.4 mmol) portionwise at -70 °C, and warmed to room temperature for 10 min, and again cooled at -70 °C for 10 min. To the mixture is added allyl bromide (266 mg, 2.2 mmol) dropwise and warmed to -10 °C for 1 h,<sup>9)</sup> then 50 °C for 30 min. The mixture is treated with sat. aq.  $NH_4OH$  and is extracted with ether. After usual work-up, the product is chromatographically (SiO<sub>2</sub>) purified to give the allyl-thionolactone

				Tabl	e 1.				
Substrate	Allyl halide	Product	Ratio <sup>a)</sup> (anti:syn)	Yield %	Substrate	Allyl halide	Product	Ratio <sup>a)</sup> (anti:syn)	<u>Yield</u> %
H OS BnO <u>1</u>	≁Br <u>3a</u>	H OS BnO <u>5a</u>	1.1:1	85.5	BnO 2	<u>3a</u>	H O S BnO <u>6a</u>	3.5:1	79.2
<u>1</u>	<u></u> B: _ <u>3b</u>	r H OS BnO <u>5b</u>	1.3:1 <sup>b)</sup>	70.0	2	<u>3b</u>	H OS BnO <u>6b</u>	b),c)	77.9
<u>1</u>	<u>3c</u>	H OS BnO <u>5c</u>	X=Br 2.2:1 X=C1 2.0:1	25.0 31.6	2	<u>3c</u>	HUOS BnO <u>6c</u>	X=Cl 3.2:1	14.6
<u>1</u>	<u> </u>	H, OS Bno <u>5d</u>	3.2:1	8.0	2	<u>3d</u>	Hydre <u>6d</u>	4.4:1	52.0
<u>1</u>	IOBI	n H BnO <u>5e</u>	1.4:1 <sup>b)</sup>	39.3	2	<u>3e</u>	Bno <u>6e</u>	4.4:1 <sup>b)</sup>	52.0
H BnO 5a	<u>3a</u>	HOS <u>9a</u>		82.7	<u>5a</u>	<u>3c</u>	H O S <u>9c</u>	X=Cl 1.0:0	15.3
<u>5a</u>	<u>3b</u>	H OS <u>9b</u>	b),c	;) 61.6	H H H OS BnO <u>5k</u>	<u>3a</u>	HHOS <u>9b</u>	c)	50.7

(5	$R_{1} = R_{2} = H_{1}$	448	mg,	85.5%)	as	а	<u>syn</u> /	anti	mixture.
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a) Determined by HPLC (EYELA PLC-10, Microsorb (80-115, 4.6 mm x 150 mm), 2% <sup>1</sup>PrOH-hexane) and <sup>1</sup>H-NMR. b) Stereochemistry and relative ratio of the newly generated allylic center could not be determined. c) Ratio could not be determined.

## References

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- 9) Cf. S. Takano and K. Ogasawara, Yuki Gosei Kagaku Kyokai Shi, <u>40</u>, 1037 (1982).
- 10) Formation of a ketene thioacetal intermediate may be discernible on a silica gel TLC plate.

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