REGIOSELECTIVE THIO-CLAISEN REARRANGEMENT *via* S-ALLYL KETENE-S,N-ACETALS GENERATED FROM CYCLIC S-ALLYLMONOTHIODICARBOXIMIDE SALTS[1]

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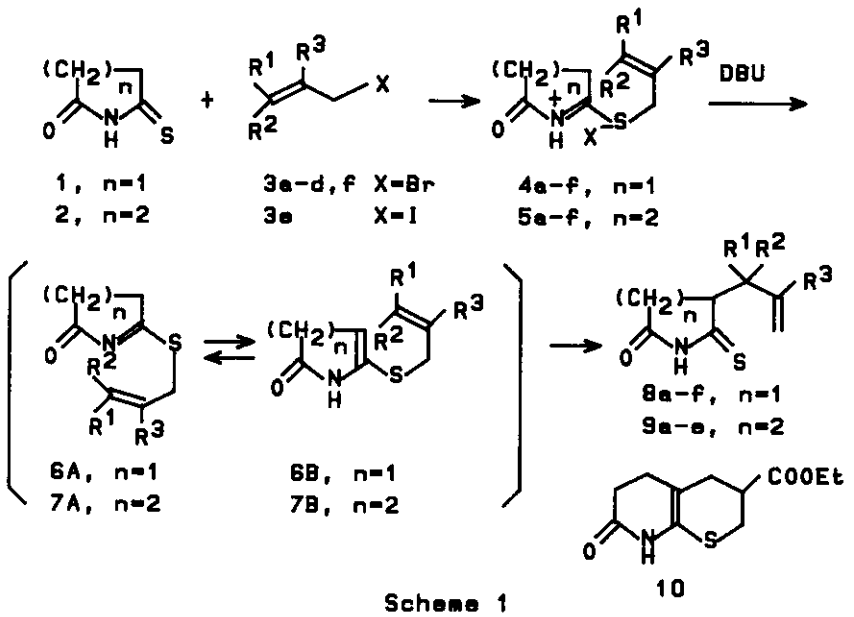
Abstract - Thio-Claisen rearrangement *via* S-allyl ketene-S,N-acetals generated from cyclic S-allylmonothiodicarboximide salts with a base furnished the S→C allylic rearranged products exclusively.

The [3,3]-sigmatropic rearrangements are one of the most important transformations in the arsenal of modern synthetic organic chemistry.[2] Although thio-Claisen rearrangement of S-allylthioimidates has been well investigated[3], no report has dealt with a study of the rearrangement in *S*-allyl-*N*-acylthioamide system. In connection with our research on organic synthesis using thioamide functions[4], we wish to communicate herein the regioselective thio-Claisen rearrangement *via* S-allyl ketene-S,N-acetals generated from cyclic S-allylmonothiodicarboximide salts with a base.

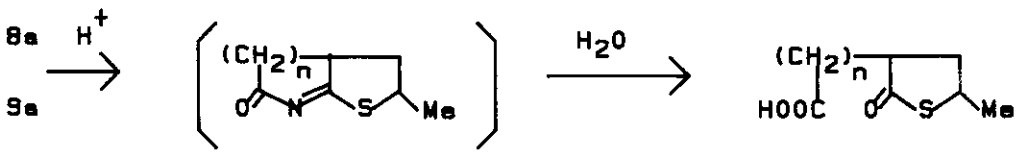
The formation of cyclic S-allylmonothiodicarboximide salts (**4a-f** and **5a-f**) by the reaction of cyclic monothiodicarboximides (**1** and **2**) with allyl halides (**3a-f**), followed by dehydrohalogenation with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) *underwent the selective S→C allylic rearrangement* to yield cyclic allylmonothiodicarboximides (**8a-f** and **9a-e**), respectively (Table 1). The reaction of **5f** gave bicyclic compound (**10**), which would be obtained by the intramolecular Michael reaction of **9f**. No traces of S→N allylic rearranged products were detected. Accordingly, the thermal rearrangement of the S-allyl ketene-S,N-acetal tautomer (**6B** or **7B**) to the C_3-allyl monothiodicarboximide (**8** or **9**) would be a faster process than that of direct rearrangement of S-allylimidate tautomer (**6A** or **7A**) to N-allylmonothiodicarboximide or the exclusive rearrangement may proceed due to the predominance of the tautomer (**6B** or **7B**) over **6A** or **7a** form in the equilibrium drawn in Scheme 1. Although it was reported palladium-catalyzed rearrangement

of cyclic S-allylthioimidates produced the S→N allylic rearranged products exclusively due to the further coordination of Pd (II) to the nitrogen atom after the coordination of Pd (II) to the allylic double bond,[3c,e] the reaction using **4a** and **5a** in the presence of Pd (II) as a catalyst gave no S→N allylic rearranged products. Because of a conjugation between the adjacent carbonyl and imine, the nitrogen might be unable to coordinate Pd (II).



Scheme 1

In order to demonstrate the synthetic utility of allylmonothiodicarboximides thus prepared, proton-induced imino thiolactonization[5] was carried out. The imino thiolactonizations of **8a** and **9a** with H_2SO_4 in HCOOH followed by hydrolysis produced the thiolactone-3-carboxylic acids (**11** and **12**),[6] respectively (Scheme 2).



Scheme 2

11, n=1 51%

12, n=2 62%

Table 1. The S → C rearranged allylic products (**8a-f**, **9a-e**, and **10**)[a)]

Product[b)]	R^1	R^2	R^3	Yield (%)	Mp (°C)	^{1}H-NMR (NH)/ppm
8a	H	H	H	67	174-177	10.1
8b	CH_3	CH_3	H	34	89-91	9.73
8c	C_6H_5	H	H	35[c,d)]	oil	9.97 10.2
8d	H	H	Br	37	65-68	10.5
8e	H	H	CH_3	40	56-60	9.93
8f	H	H	$COOC_2H_5$	66	oil	10.6
9a	H	H	H	72	71-73	9.73
9b	CH_3	CH_3	H	52	77-79	9.56
9c	C_6H_5	H	H	49[d,e)]	102-107	9.94
9d	H	H	Br	54	106-108	9.91
9e	H	H	CH_3	43	77-78	9.47
10	H	H	$COOC_2H_5$	54	111-114	8.73

a) All reactions were carried out as follows. Allylation of **1** and **2** was carried out in t-BuOH for 15 h at room temperature and subsequent dehydrohalogenation was in situ done for 4 h under reflux.

b) All new compounds were fully characterized spectroscopically (IR, 1H-NMR, and MS spectral) and by combustion.

c) A mixture of erythro:threo (5:6).

d) Stereoisomer ratios determined by 1H-NMR spectroscopy.

e) A mixture of erythro:threo (1:3).

In summary, this rearrangement proceeded regioselectively with a milder condition compared with that of S-allylthioimidates, providing the S → C rearranged products, which may be used for the further elaboration.

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REFERENCES AND NOTES

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6. Compound **11**: amorphous; ^{1}H NMR ($CDCl_3$) δ: 1.48 (3H, d, J=6 Hz, Me), 9.29 (1H, br s, COOH); IR ($CHCl_3$) ν: 1720, 1700 cm^{-1}; Mass 155 (M^+).
   Compound **12**: mp 65-67 °C; ^{1}H NMR ($CDCl_3$) δ: 1.47 (3H, d, J=6.5 Hz, Me), 9.20 (1H, br s, COOH); IR ($CHCl_3$) ν: 1700, 1690 cm^{-1}; Mass 169 (M^+).

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