THERMAL [3,3]SIGMATROPIC REARRANGEMENT OF VARIOUS ALLYLIC
THION-ESTERS. THE STRUCTURE-REACTIVITY RELATIONSHIP[1]

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Over the years [3,3]sigmatropic rearrangements have held the attention of both physical and synthetic organic chemists.[2] Recently [3,3]sigmatropic rearrangements of allylic thion-esters (eq 1) have proved to be exceedingly useful for the stereoselective construction of unsaturated systems.[3-6] However, the factors which determine the rate of rearrangement of allylic thion-esters are not well understood because in practice allylic thion-esters are not isolated, but undergo rearrangement _in situ_ to the rearranged product in one operation.

Herein we wish to report the structure-reactivity relationship for the particular [3,3]-sigmatropic variant based on the kinetical studies. The systems for study are allylic dithio-carbamate (1);[3] thionocarbamate (2);[4] and xanthate (3).[5] Furthermore, to gain an understanding of the differing reactivities of these structurally related compounds, we have carried out the simple molecular orbital (HMO) calculations.

$$ (1) $$

1, X=S, Y=NMe$_2$
2, X=O, Y=NMe$_2$
3, X=O, Y=SMe
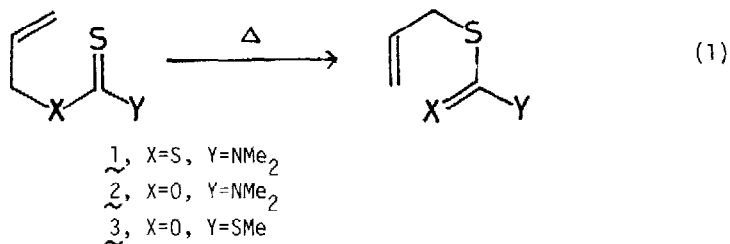
Allylic thion-esters studied here are listed in Table 1. All the thion-esters were prepared by the published procedures and carefully purified.[7] In preliminary experiments, we found that the allylic thion-esters were converted quantitatively in refluxing toluene into the corresponding thiol-esters in which the allylic groups were stereospecifically rearranged, as required by an electrocyclic mechanism as described in Table 1. The rearrangements produced changes in the NMR patterns in the predictable manner.[8]

Thus the rearrangements of these thion-esters were followed in bromobenzene by NMR spectroscopy. All reactions were found to be of first order to at least 60% conversion.

Table 1 shows the relative rate constants (k_r) thus obtained.

Of great interest in Table 1 are the striking dependences of the rate of rearrangement (k_r) on both the structure of the thion-ester part and the methyl substitution on the allyl part; (a) the effect of the thion-ester on k_r : OC(S)SMe (3) > SC(S)NMe$_2$ (1) > OC(S)NMe$_2$ (2); (b) the effect of methyl substitution on k_r : α-Me > γ-Me > unsubstituted. These orders unequivocally indicate that the k_r-value is not dependent upon the magnitude of the energy gap between the substrate and the product ($\Delta E_A + \Delta E_S$) in view of the order of ($\Delta E_A + \Delta E_S$) described in Table 1.

In order to establish the factors determining the rate of rearrangement, we carried out the HMO calculations using appropriate parameters[9] to give the π-bond order (p) and the π-electron density (q) on the thion-ester parts. The selected values thus obtained were relatively comparable to those reported by Janssen[10] using different parameters (Table 2).
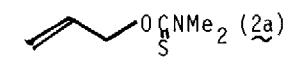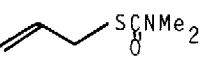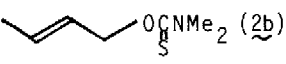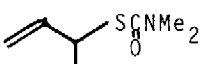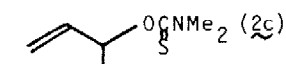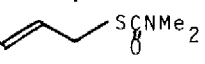
Comparison of the calculated values with the kinetical data reveals that the rate of rearrangement increases with an increase in the π-bond order of the C=S (p_{C-S}), indicating that an interaction between the two π orbitals of the C=S and C=C bonds plays an important role in determining the rate. This correlation of k_r with p_{C-S} allows not only an understanding of 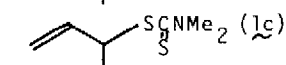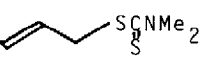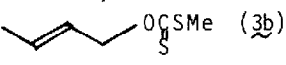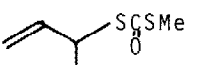the differences in the reactivity of allylic thion-esters but also a prediction of the relative rate of rearrangement of other thion-esters. For instance, p_{C-S} for trithiocarbonate (X=S, Y=SMe) was calculated to be 0.840 (by Janssen[10]), leading us to predict that allylic trithiocarbonate might be rearranged faster, at least comparably, than the xanthate analog 3. It should be noted that the k_r-value for the thion-ester series also increases with decreasing the π-electron density on the thion-sulfurs, suggesting that π electrons might move more favorably from the allyl part to the thion-ester part on passing to the transition state.

Finally, the effect of methyl substitution on the allyl part on k_r described above can be explained by essentially the same arguments used to rationalize the similar effects of methyl substitution observed in the [3,3]sigmatropic rearrangements of allyl phenyl ethers[11] and allyl phenyl thionocarbonates.[6b] The transition state (4) assumed for rearrangement of thion-esters
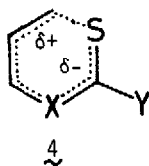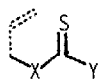
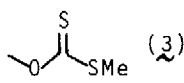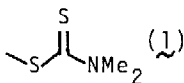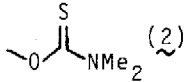should be more polar than the thion-ester itself since mutual conjugation between the allyl and the thion-ester parts should lead to polarization of the delocalized electrons in the aromatic,[12] pericyclic ring. Thus the increased positive charge on the allyl part on passing to the transition state (4) is correspondingly stabilized by the methyl substitution on the allyl part, resulting in an increase in the rate of rearrangement.

Table 1   [3,3]Sigmatropic Rearrangements of Allylic Thion-esters[a]

Substrate ⟶ Product		Rel. k_r	Gain in stabilizing energy[b]
$O\overset{S}{\underset{}{C}}NMe_2$ (2a)	$S\overset{O}{\underset{}{C}}NMe_2$	1.0^c	ΔE_S
$O\overset{S}{\underset{}{C}}NMe_2$ (2b)	$S\overset{O}{\underset{}{C}}NMe_2$	5.0	$\Delta E_S - \Delta E_A$
$O\overset{S}{\underset{}{C}}NMe_2$ (2c)	$S\overset{O}{\underset{}{C}}NMe_2$	40	$\Delta E_S + \Delta E_A$
$S\overset{S}{\underset{}{C}}NMe_2$ (1c)	$S\overset{S}{\underset{}{C}}NMe_2$	240	ΔE_A
$O\overset{S}{\underset{}{C}}SMe$ (3b)	$S\overset{O}{\underset{}{C}}SMe$	480	ΔE_S

[a] All runs were carried out under the conditions: concn., 0.74 mol/l; solvent, bromobenzene; temp., 80.5±0.5°C. [b] ΔE_A and ΔE_S refer to the stabilizing energies gained on going from the monosubstituted to the disubstituted olefin and from the thion-ester to the thiol-ester, respectively, the magnitudes of ΔE_A and ΔE_S depending upon the structure of the thion-esters. [c] k_r(obs) = 6.7 x 10^{-5} min^{-1}.

Table 2   HMO Calculations of the Thion-esters

$\underset{X}{\overset{S}{\underset{}{\|}}}\,{}_Y$	Rate of Rearrangement	π-Bond order of the C=S bond (p_{C-S})[a]	π-Electron density of the thion-sulfur (q_s)[a]
$\underset{O}{\overset{S}{C}}SMe$ (3)	Fast	0.837 (0.801)	- 0.473 (- 0.454)
$\underset{S}{\overset{S}{C}}NMe_2$ (1)	Medium	0.715 (0.732)	- 0.598 (- 0.535)
$\underset{O}{\overset{S}{C}}NMe_2$ (2)	Slow	0.570 (0.687)	- 0.914 (- 0.604)

[a] These values were obtained in this work using Pullman's parameters (ref 9) described below. The values in parentheses are those reported by Janssen (ref 10) using the parameters in parentheses described below.

Coulomb integral (α_x): (C)=S, $\alpha + 0.9\beta$ ($\alpha + 0.5\beta$); -S-, $\alpha + 0.9\beta$ ($\alpha + 1.0\beta$); -O-, $\alpha + 2\beta$ ($\alpha + 2.5\beta$); -N<, $\alpha + 1.0\beta$ ($\alpha + 1.5\beta$). Resonance integral (β_{C-x}): C=S, $1.2\beta(1.0\beta)$; -S-, 0.5β (0.6β); -O- 0.6β (1.2β); -N<, 1.0β (1.2β).

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7) All the thion-esters were purified by high-vacuum distillation at 50-70°C except for 1c (by column chromatography) and were not contaminated with the rearranged products except for 2c which was obtained as a mixture of 2c (90%) and the rearranged product (10%).

8) For example, the NMR spectrum (PhBr, TMS) of 2c exhibited a doublet at $\delta 1.4$ (α-Me) and two singlets at $\delta 3.1$ and 3.2 (NMe_2) whereas that of the rearranged thiol-ester showed a doublet at $\delta 1.7$ (γ-Me) and a singlet at $\delta 3.0$ (NMe_2).

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