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Study of the Thio-Claisen Rearrangement. Rearrangement of 2-Allylthiobenzothiazole and Related Compounds

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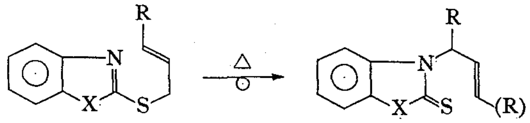
2-Allylthiobenzothiazole underwent thermal rearrangement to N-allylbenzothiazoline-2-thione. Positional deuterium labeling on the allylic moiety indicated the inversion of the allylic moiety in this rearrangement. The study of the secondary deuterium kinetic isotope effect and the kinetic solvent effect were compatible with a concerted "Thio-Claisen" pathway through a transition state of a very low polar character.

INTRODUCTION

Recently, molecular rearrangements of a class of compounds in which the heteroatoms reside at both the migration origin and the migration terminus drew much attention. Among these reactions, the Chapman rearrangement (O→N rearrangement) and the Schönberg rearrangement (O→S rearrangement) were recently reviewed.[1)]

We have presented some of the examples of such a rearrangement. One of the characteristics of these reactions was a nucleophilic attack of the heteroatom in a concerted cyclic transition state.[2)]

In the present paper, we present a study of the thermal rearrangement of 2-allylthiobenzothiazole to N-allyl benzothiazoline-2-thione and the rearrangement of the corresponding benzimidazole and benzoxazole as is shown in Scheme 1.



(I) (II)

X=S, O, NCH_3. R=H, D.

Scheme 1

In contrast to the apparent similarity to the Claisen rearrangement, such a class of the compound involves a potential complexity inherent to an allylic sulfide of a heteroaromatic series. Possible pathways leading to II ("Claisen" product) and to III ("Chapman"

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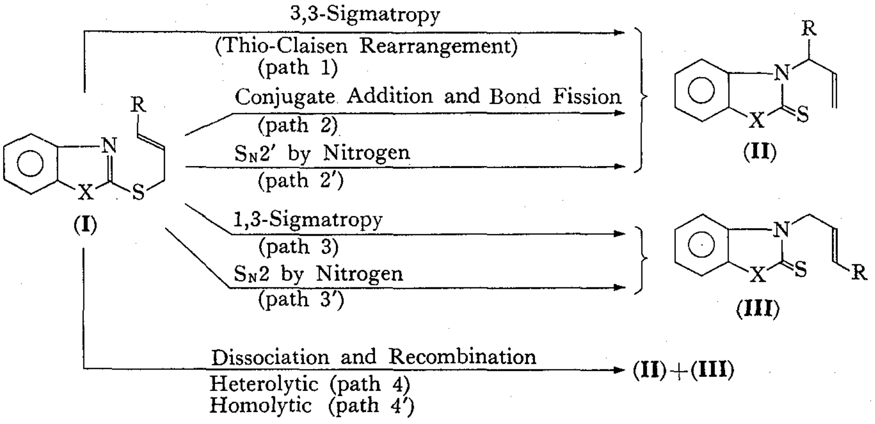
product) are as follows.*



Scheme 2

Path 1 (thio-Claisen rearrangement) and path 3 are concerted sigmatropic rearrangements while path 2 (Michael type conjugate addition and bond fission), path 2′ (S_N2') and path 3′ (S_N2) are polar intramolecular nucleophile displacement. Dissociation and recombination mechanism such as path 4 and path 4′ also should be taken into consideration.

These allylic sulfides were first studied in 1952 by Moore and Waight. In their pioneering work,[3] they have shown that these reactions were reversible and they suggested the duality of the mechanism, namely, the competition of the concerted thio-Claisen rearrangement (path 1) and the fragmentation-recombination *via* an ion-pair intermediate (path 4).

However, the British authors had presented no evidence that precludes the possibility of other processes.

In the present work, in a trial to distinguish these possibilities, we describe the study with deuterium labeling and with the kinetic solvent effect.

RESULTS

2-Allylthiobenzothiazole (Ia) and its deuterated analogues (Ib and Ic) were prepared** by the displacement reaction in Scheme 3 and were subjected to the thermal rearrangement. Similarly 2-allylthiobenzoxazole (Id) and 1-methyl-2-allylthiobenzimidazole (Ie) were prepared.***

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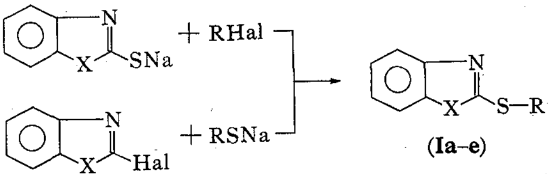
* In this and the subsequent paper, the rearrangement product with the "inversion" in the allylic moiety will be called "Claisen" product. And the product with the "retention" in the allylic moiety will be called "Chapman" product. These names stem from the apparent identities of the product but do not necessarily signify the real pathway through which the product was formed.

** The result with deuterated allyl chlorides showed that there was negligible participation of S_N2' pathway in the course of the preparation of this allylsulfide. Deuterated compounds (Ib and Ic) contained 1.87 and 1.85 atom D per specified methylene group respectively.

*** In this paper, the general name "benzazole" was used for the abbreviation of such bicyclic azoles, benzothiazole (Ia), benzoxazole (Id), and benzimidazole (Ie).



(Ia–e)

Ia; X=S, R=allyl: Ib; X=S, R=allyl-1, 1-d_2: c; X=S, R=allyl-3, 3-d_2:
d; X=O, R=allyl: e; X=NMe, R=allyl:
Hal=Cl, Br
Scheme 3

Upon heating the neat sample in a nitrogen atmosphere, 2-allylthiobenzothiazole (Ia) gave N-allylbenzothiazoline-2-thione in an excellent yield at 170–200°C. Even at 230°C, Ia rearranged smoothly with little tendency to decompose, and both the deuterated compounds, 2-(allyl-1′,1′-d_2-thio)-benzothiazole (Ib) and 2-(allyl-3′,3′-d_2-thio)-benzothiazole (Ic), gave the rearranged product with virtually complete inversion of the allylic moiety. This was proved by the NMR measurement.

Other 2-allylthiobenzazoles (Id,e) underwent similar rearrangement to give N-allylbenzazoline-2-thiones (IId,e).

Rates of rearrangements of 2-allylthioazoles Ia, b, c in a variety of solvents were followed spectrophotometrically with the aid of an ampoule technique.

The first-order kinetics was followed in every case as shown in Figs. 1, 2, and 3. First-order rate coefficients in a variety of solvents are summarized in Table I. As there is a possibility of solvent-dependent variation of equilibrium constants for azole-azoline rearrangement, initial rate constants were utilized in the study of the kinetic solvent effect.*

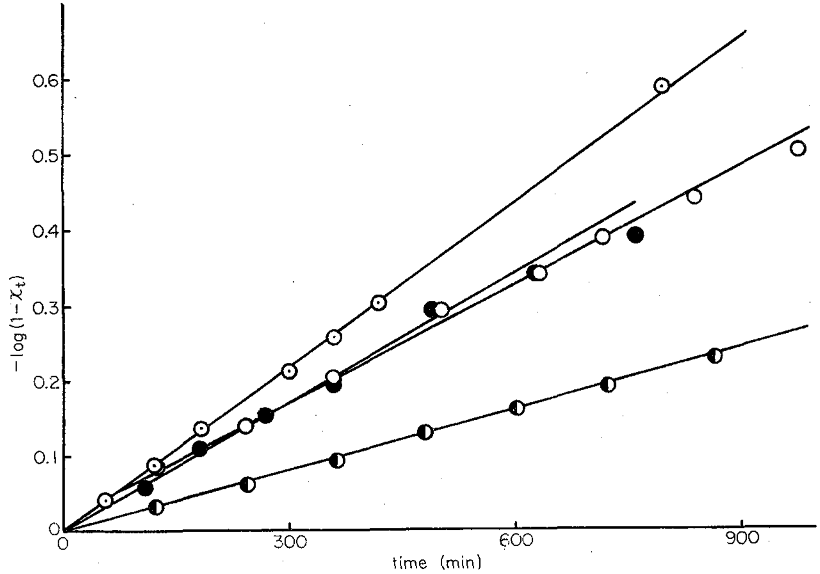


Fig. 1. Rate plots for the rearrangement of Ia in aprotic solvents, THF (○, Z=71.6), acetonitrile (◎, Z=71.3), acetone (●, Z=65.5), and iso-octane (◐, Z=60.1), at 170°C.

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* Differences between the initial rate constants (k_{init}) and the rate constants for the forward process (k_1) were not large (2–3% or less) for the present reactions as is shown in Tables I and II. The formex was slightly smaller than the latter.

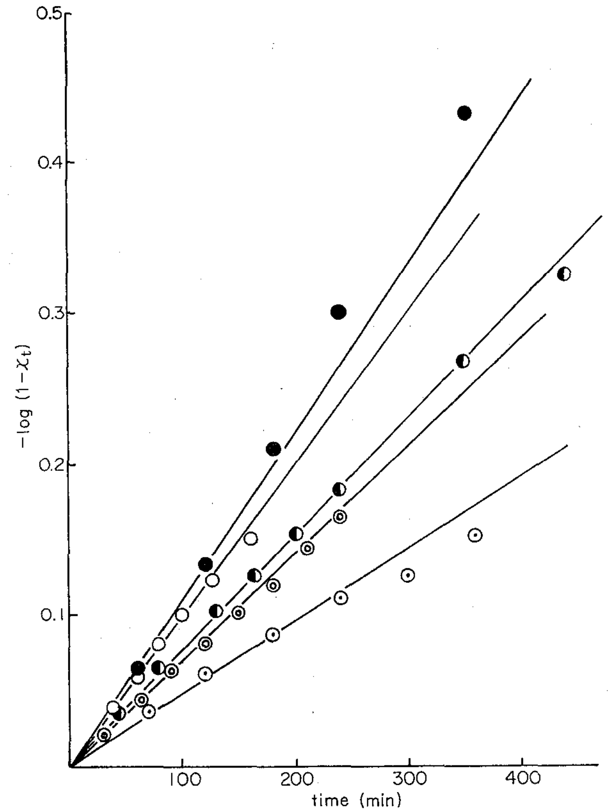

Fig. 2. Rate plots for the rearrangement of Ia in protic solvents, ethyleneglycol (●, Z=85.1), ethanol-water (4 : 1) (○, Z=84.8), Carbitol (◐, Z=78.1), ethanol (◎, Z=79.6), and isopropanol (⊙, Z=76.3), at 170°C.

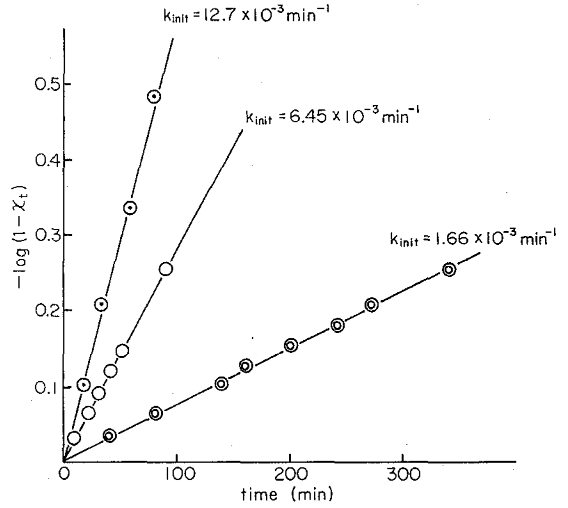

Fig. 3. Rate plots for the rearrangement of benzozales, 2-allylthiobenzothiazole (Ia, ◎), 2-allylthiobenzoxazole (Id, ○), and 1-methyl-2-allylthiobenzimidazole (Ie, ⊙), in Carbitol at 170°C.

For the discussion of secondary kinetic deuterium isotope effect, the kinetic data in acetonitrile were solely utilized, where equilibrium constants were estimated from the rate of the forward and the reverse reactions. The results are shown in Tables II and III.

DISCUSSION

Recently, Makisumi and Sasatani have reported a similar thio-Claisen rearrangement, thus there established a reversible isomerization between 2-alkenyl 2′-quinolyl sulfide and N-2′-alkenylthiocarbostyrils, with the profound preference (more than 90%) of the former in their equilibrium.[4] However, essentially no evidence was presented to show the nature of the reaction.

Examples of the thio-Claisen rearrangement with a carbon as a migration terminus were reported[5] with the other example of sulfur to nitrogen rearrangement. 3,3-Sigmatropic process was inferred to these reactions only by the product analyses and by low negative entropy of activation.

In the present study, our results reconfirmed the activation parameters reported by Moore and Waight.[3] Low negative entropies of activation observed in the present study are compatible with the cyclic transition state.

Thermal rearrangements of the deuterated compounds at 230°C demonstrated the inversion of the allylic moiety in the rearrangement of 2-allylthiobenzothiazole (Ia b,c). These results preclude the intervention of the allylic carbonium ion or of the allylic free radical.

The product analyses, thus, favor path 1, path 2, or path 2′ over path 3, path 3′, path 4 or possibly path 4′.

In a recent paper, White and Wolfarth had pointed out that there is a reasonably good correlation between the Kosower's Z values[6] and the rates of rearrangement of allyl p-tolyl ether in a variety of solvents.[7] And a dipolar or a charge-separated transition state was ascribed in the Claisen rearrangement of these allyl ethers.

As is shown in Fig. 4, the rate data in Table I gave a reasonable correlation with Kosower's Z value in the following equation, the sensitivity to solvent polarity being

$$Z=39.58(\log k+4)+28.69 \quad (r=0.899)$$

less than half in 2-allylthiobenzothiazole compared with that in allyl p-tolyl ether.*

Very low sensitivity to solvent polarity can best be rationalized by a very low charge separation in the transition state. Accordingly, paths 2, 2′, and 4 all of which contain polar transition state should be excluded.

Rates of the Menschutekin reaction, which involves the nitrogen nucleophile, is similarly insensitive to Z value in a variety of monohydric alcohols.[6] However, rates of such a polar bimolecular substitution are highly affected by the change of the reaction medium from protic to dipolar aprotic.[8] Such a significant change was not observed in the present study thus showing very little polar nature of the rearrangement studied.

Secondary deuterium kinetic isotope effect was determined for 2-allylthiobenzothiazole

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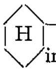
* White and Wolfarth presented the relaitonship

$$Z=15.93(\log k+6)+58.79 \quad (r=0.892)$$

for the rearrangement of allyl p-tolyl ether.[7]

Table I. Solvent Effect

Rearrangement Rate Constants k_{init} for Compound Ia at 170.0±0.05°C.

Run	Solvent	$k_{init} \times 10^4$ min^{-1}	Z
1	iso-Octane	6.177	60.1
2	THF	11.84	71.6[a]
3	Acetone	12.04	65.5
4	CH_3CN	16.31	71.3
5	i-PrOH	11.56	76.3
6	Carbitol	16.50[b]	78.1
7	EtOH	16.38	79.6
8	$EtOH/H_2O(8:2)$	23.41	84.8
9	Ethylene Glycol	27.74	85.1
10	$ClN(Et)_4$ (1.52M) in CH_3CN	15.35	
11	 $-CH_3$ (1.0 mol) in CH_3CN	15.63	

a) Calculated from $Y_{THF}=-6.073$ by tentatively assuming $Y=0.41632Z-35.877$. c.f. E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958).

b) $E_a=30.4$ Kcal/mole and $\Delta S^{\ddagger}=-13.6$ e.u. (at 170°C) were obtained from $k_{init}^{160}=7.53\times10^{-4}$, $k_{init}^{180}=38.53\times10^{-4}$ and $k_{init}^{200}=167.2\times10^{-4}$ (min^{-1} respectively).

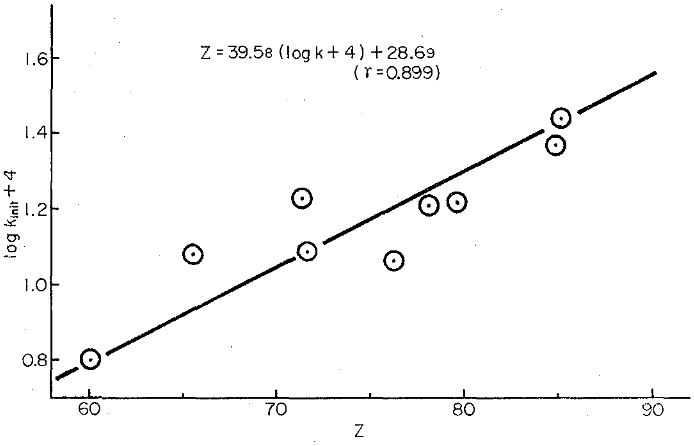


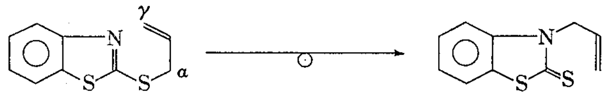
Fig. 4. Kinetic solvent effect. Plot of log k_{init} and Kosower's Z.

in acetonitrile at 170° and 190°C. The results are shown in Table II. The magnitude of the effect represented as k_H/k_D per one deuterium atom is close to unity. This is an additional support to the concertedness of the reaction mechanism.[9]

However, the general trend observed in the present study is without precedent. 2-Allylthiobenzothiazole showed about 2–3% of the inverse effect at the α-position to the sulfur and about 4–5% of the normal effect at γ-position to the sulfur atom, the migration origin.

Other allylic rearrangements which are believed to proceed via a concerted mechanism show normal isotope effect that amount about 7–10% at the bond-breaking α-position and

Table II. Isotope Effect in the Rearrangement of 2-Allylthiobenzothiazole in Acetonitrile.



Solvents	Temp.[a] (°C)	$k_{2H} \times 10^4$ (min^{-1})	$k^{b)}_{\alpha-2D} \times 10^4$ (min^{-1})	$k^{b)}_{\gamma-2D} \times 10^4$ (min^{-1})	$k_{2H}/k_{\alpha-2D}$	$k_{2H}/k_{\gamma-2D}$
acetonitrile	190.0	75.70	81.27	—	0.931	—
	190.0	76.86	—	70.18	—	1.095
	170.0	16.72	17.71	15.14	0.938	1.097
	170.0	16.72	17.58	15.55	0.958	1.083

a) Temperature was controlled to the variation of ±0.05°C or better.

b) $K^{190}_{H}=12.32$, $K^{190}_{\alpha-D}=12.17$, $K^{190}_{\gamma-D}=12.47$

$K^{170}_{H}=13.88$, $K^{170}_{\alpha-D}=13.61$, $K^{170}_{\gamma-D}=13.71$

These equilibrium constants were estimated from the initial rate constant for the forward and reverse reaction. Observed rate constants for the deuterium content 1.87D (1.85D) were corrected to the rate constants for the fully deuterated compound by the standard method. c.f. S. Seltzer, *J. Amer. Chem. Soc.*, **83**, 2626 (1961).

also show inverse isotope effect of about 2–3% at the bond-forming γ-position.[9a)] Sunko has discussed the implication of the isotope effect upon the relative position of the transition state on the reaction coordinate.[9b)]

The isotope effects obtained in the present work are hard to be interpreted. One possible explanation of the inverse isotope effect may be found in the hyperconjugative stabilization of the ground state, sulfur atom *α* to the methylene serves as an electron acceptor.[10)] Hyperconjugative stabilization is more effective for hydrogen than for the deuterium,[11)] and is in accord with the observation.

Normal isotope effect of the terminal methylene group can probably be ascribed to the homo-conjugation involving the sulfur atom. Electron donating inductive effect of the deuterium on the terminal methylene is more effective[11)] than that of the hydrogen thus promoting the interaction of allylic double bond with the sulfur atom, here also the sulfur atom being the electron acceptor.

The effect of the hetero-atom in the azole ring is interesting. Thus heteroatom in 2-allylthiobenzazole rings facilitates the rate of the "Thio-Claisen" rearrangement in the following order; -NMe>-0->-S-. This trend may be a manifestation of the increased electron density or electron mobility of the azole system which is most probably one of the driving force of the rearrangement.

Product analyzed, activation parameters, kinetic solvent effect, and secondary kinetic isotope effect are all in accord with the concerted mechanism with a very little charge separation at the transition state. Thus the thermal rearrangement of 2-allylthiobenzothiazole should be regarded as a thio-analogue of the Claisen rearrangement with a six-membered cyclic transition state rather than as the thio-Chapman rearrangement.

EXPERIMENTAL

NMR spectra were determined with a JEOL's C60-HL sepectrometer operated at 60 MHz using $CDCl_3$ as the solvent unless otherwise stated. Peak positions are expressed in p.p.m. from the internal standard tetramethylsilane. Ultraviolet absorption spectra were obtained in $CHCl_3$ (generally ca. 10^{-4} M soln) with a Shimadzu QV-50 spectrophotometer and the wave-length is expressed in nm. Infrared spectra were taken with a JASCO DS-402G grating spectrophotometer as KBr pellet or a liquid film. Absorption maxima are expressed in wave numbers (cm^{-1}). All melting points were measured with a Shimadzu-Unimelt apparatus and were uncorrected.

Materials: General method of the preparation of the allylthiobenzazoles was given in Scheme 3.

2-**Allylthiobenzothiazole (Ia).** To a solution of sodium ethoxide (from 2.5 g of sodium metal) in 70 ml of ethanol was added 17.0 g (0.10 mole) of 2-mercapto-benzothiazole in small portions. To this solution, 13.0 g (0.11 mole) of allyl bromide in 30 ml of ethanol was added dropwise at 0–10°C under effective stirring. After the addition was completed, the mixture was stood at room temperature overnight. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was poured into ca. 100 ml of cold water and was extracted with three 50 ml portions of ether. The ethereal extract was dried with anhydrous magnesium sulfate and was concentrated under reduced pressure. Crude material thus obtained was distilled at 123°C (0.02–0.03 mm Hg) to give 18.5 g (89%) of colorless liquid (lit.[3] 126–9°C at 0.05 mmHg): λ_{max} 282(1.329×10^4); δ 3.98 (d) ($-CH_2-$), 5.13 (m) ($=CH_2$), 5.75 (m) ($-CH=$)

Anal. Calcd for $C_{10}H_9NS_2$: C, 57.93; H, 4.38; S, 30.94
Found: C, 58.21; H, 4.46; S, 30.75

2-**Allylthiobenzoxazole (Id).** To a sodium ethoxide solution prepared from 0.305 g (0.013 mole) of sodium metal and 20 ml of ethanol was added 1.2 g (0.015 mole) of allyl mercaptan (propene-3-thiol). To the resulting solution, 2.0 g (0.013 mole) of 2-chlorobenzoxazole in 10 ml of ethanol was added in portions. The addition was controlled at such a rate that the temperature never exceeded 15°C. The resulting mixture was left overnight with stirring at a room temperature. The work-up was made as described for Ia and the distillation at 105–107°C/0.55 mmHg gave 1.85 g (74%) of colorless liquid: λ_{max} 280 (1.312×10^4); IR 1641, 925; δ 3.90 (d) ($-CH_2-$), 5.80 (m) ($=CH_2$), 5.87 (m) ($-CH=$)

Anal. Calcd for $C_{10}H_9NOS$: C, 62.80; H, 4.74; S, 16.77
Found: C, 62.83; H, 4.59; S, 16.65

N-Methyl-*2*-allylthiobenzimidazole (Ie). To a solution of sodium N-methylbenzimidazole-2-thiolate (0.005 mole) in 50 ml of acetonitrile, equimolar amount of allyl bromide in 10 ml of acetonitrile was added dropwise at 0–5°C. The resulting mixture was stirred overnight at room temperature and filtered to remove the precipitated sodium bromide. The filtrate was concentrated in vacuo and the resulting residue was poured into ice-water. The organic layer was taken up in ether. The ethereal extract was dried with anhydrous magnesium sulfate and concentrated to give pale yellow oil. Distillation under reduced pressure gave 0.60 g (60%) of pale yellow liquid (bp. 120°C/0.05 mmHg): λ_{max} 287(1.285×10^4); IR 1635, 915; δ 3.30 (s) (NCH_3), 3.91 (d) ($-CH_2-$), 5.15 (m) ($=CH_2$), 6.05 (m) ($-CH=$)

Anal. Calcd for $C_{11}H_{12}N_2S$: C, 64.67; H, 5.92; S, 15.70
Found: C, 64.38; H, 5.97; S, 15.85

Allyl-1,1-d_2 chloride and allyl-3,3-d_2 chloride were prepared by the standard method,* and were utilized for the synthesis of the deuterated 2-allylthiobenzothiazoles (Ib and c) by the method of the synthesis of Ia. The spectroscopic data of Ib and Ic are as follows. Ib: λ_{max} 282 (1.329×10^4); IR 2170, 2105, 1041: δ 5.13 (m) (=CH_2) 5.75 (broad q) (—CH=). Inc: λ_{max} 282 (1.328×10^4); IR 2290, 2185, 1100, 845: δ 3.98 (d) (—CH_2—), 5.75 (broad t) (—CH=).

Thermal Rearrangement of the *2*-Allylthiobenzazoles (I), Product Analysis: About one gram of the neat sample of I was placed in a tube and was sealed under nitrogen. The sealed tube was heated in a thermostated bath for an appropriate time (IIa, 200°C 4hr, IIb, 200°C 6hr, IIc, 230°C 3hr; IId, 200°C 1hr; IIe, 200°C 2hr).

When the reaction was essentially over, the sealed tube was cooled and was opened. The content was chromatographed on silica-gel using benzene-*n*-hexane mixture (1 : 1) as an eluant. The purification of the product was achieved by recrystallization from *n*-hexane.

N-Allyl-benzothiazoline-*2*-thione (IIa). mp 67.5–68.0° (lit.[3]) mp 67.5–68.5°); λ_{max} 329 (2.86×10^4): δ 4.99 (d) (—CH_2—), 5.95 (m) (—CH=), 5.26 (m) (=CH_2).

Anal. Calcd for $10_{10}H_9NS_2$; C, 57.93; H, 4.38; S, 30.90

Found: C, 57.66; H, 4.56; S, 30.70

N-(Allyl-*3′*,*3′*-d_2)-benzothiazoline-*2*-thione (IIb). mp 66.0–66.5°; λ_{max} 329 (2.860×10^4); δ 5.00 (d) (—CH_2—), 5.95 (broad-t) (—CH=)

N-(Allyl-*1′*,*1′*-d_2)-benzothiazoline-*2*-thione (IIc). mp 66.5–67.0; λ_{max} 329 (2860×10^4); δ 5.93 (broad-q) (—CH=), 5.26 (m) (=CH_2).

N-Allyl-benzoxazoline-*2*-thione (IId). mp 90.5–91.0°; λ_{max} 308 (2.954×10^4); IR 1642, 925; δ 4.80 (d) (—CH_2—), 5.40 (m) (=CH_2), 5.93 (m) (—CH=).

Anal. Calcd for $C_{10}H_{12}NOS$; C, 62.80; H, 4.74; S, 16.77

Found: C, 62.72; H, 4.97; S, 16.78

1-Methyl-*3*-Allyl-benzimidazoline-*2*-thione (IIe). mp 74.8–75.5°; λ_{max} 314 (3.330×10^4); IR 1642, 912; 3.78 (s) (N-CH_3), 4.85 (d) (—CH_2—), 5.20 (m) (—CH=).

Kinetic Measurement: Rates were followed by the ampoule technique. Approximately 50 mg of I was accurately weighed and was dissolved in an appropriate solvent to make up 5 ml of about 0.05 M solution. One ml aliquots were transferred into the ampoule flushed with nitrogen. Ampoules were sealed and were heated in a thermostated bath and were withdrawn at intervals. After cooling, the reaction mixture was diluted with chloroform and was analyzed spectrophotometrically.

The mole fraction of starting material I and the product II was calculated from the absorbance at the maximum absorption of the component. Total concentration of the component ((I)+(II)) remained essentially constant within experimental error throughout the kinetic run. However, in protic solvents, some decomposition was observed as

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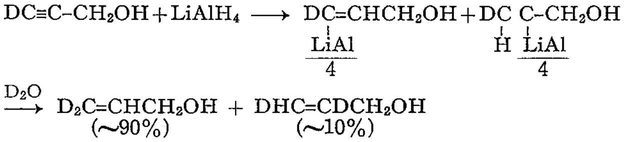
* ref. 9a. However, about 10% of the inverse addition was observed in the reaction of propyn-3-ol-1-d with lithium aluminum hydride.



$$DC{\equiv}C\text{-}CH_2OH + LiAlH_4 \longrightarrow \underset{\frac{LiAl}{4}}{DC}{=}CHCH_2OH + \underset{H}{DC}\ \underset{\frac{LiAl}{4}}{C}\text{-}CH_2OH$$

$$\xrightarrow{D_2O} \underset{(\sim 90\%)}{D_2C{=}CHCH_2OH} + \underset{(\sim 10\%)}{DHC{=}CDCH_2OH}$$

shown in Fig. 3. Initial rate constants were calculated assuming the irreversible first order reaction.

For the determination of the deuterium isotope effect, simultaneous kinetic measurements were carried out on 2-allylthiobenzothiazole (Ia) and its deuterated analog (Ib and c). The equilibrium constant of these three reactions were estimated by measuring the rates of the reverse reactions, the rearrangements of IIa, IIb and IIc. Rate constants for the rearrangement in acetonitrile were calculated by assuming the reversible first order kinetics and the excellent fits were obtained as is exemplified in Table III.

Table III. Rearrangement of 2-allylthiobenzothiazole (Ia) to N-allylbenzothiazoline-2-thione (IIa) in Acetonitrile at 170.0+0.05°C.

Time (min.)	Mole fraction of IIa (x_t)	$k_1\times10^4$ (min^{-1})[a]
0	0.0000	—
60	0.0949	16.69
120	0.1804	16.70
183	0.2602	16.67
243	0.3870	16.73
300	0.3295	16.67
360	0.4442	16.76
420	0.4932	16.71
5040[b]	0.9328	—

a) Calculated as a reversible first-order reaction using

$$(k_1+k_{-1})=\frac{2.303}{t}\log x_e/(x_e-x_t),$$

x_e being 0.933.

b) This (infinite) value is in good agreement with the calculated value from

$$k_{init}^{forward}/k_{init}^{reverse}=16.31\times10^{-4}(min^{-1})/1.71\times10^{-4}(min^{-1}).$$

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