814. 2-*Mercaptobenzothiazole Derivatives. Part II.* The Thermal Decomposition and Isomerisation of 2-Alkyl- and 2-Alkenyl-thiobenzothiazoles and 3-Alkyl- and 3-Alkenyl-2-thiobenzothiazolines.*

By C. G. Moore and E. S. Waight.

A study of the thermal treatment of variously constituted 2-alkyl- and 2-alkenyl-thiobenzothiazoles (I) and 3-alkyl- and 3-alkenyl-2-thiobenzothiazolines (II) reveals that two reaction courses are operative : (i) the thermal isomerisation of (I) to (II), which is reversible when R = alkenyl; and (ii) the thermal decomposition of (I) to 2-mercaptobenzothiazole (III) and a hydrocarbon derived from R by loss of hydrogen. Examples of the sole operation of (i) and (ii) are found in the cases of (I; R = allyl, *cyclo*hexyl respectively). All the other compounds studied show mixed reaction characteristics. A kinetic study of the decomposition or reversible isomerisation of (I; R = *cyclo*hexyl, allyl, and *cyclo*hex-2-enyl) indicates that the reactions are of the first order. The mechanisms of the decompositions and isomerisations are discussed and the relation of the reversible isomerisations of (I) and (II) (R = alkenyl) to the Claisen and analogous rearrangements is detailed.

The isolation of 2-(*cyclo*hex-2-enylthio)benzothiazole (I; R = *cyclo*hex-2-enyl) and 3-(*cyclo*hex-2-enyl)-2-thiobenzothiazoline (II; R = *cyclo*hex-2-enyl) in equilibrium proportions (Part I *) necessitated a study of the pyrolysis of these and related compounds in order to determine the factors influencing their relative tendencies towards isomerisation and decomposition.

This paper is concerned with the thermal treatment of compounds of types (I) and (II) in which the substituent R is alkyl, aralkyl, and alkenyl. Previous studies in this field have

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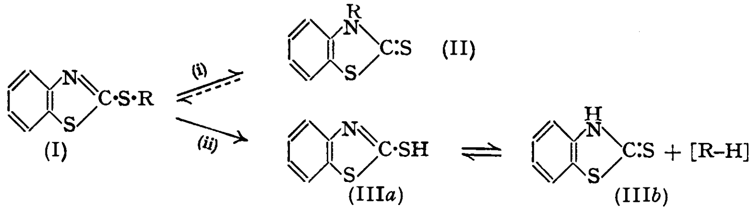
* Part I, preceding paper.

been made by Reed, Robertson, and Sexton (*J.*, 1939, 473) and by Fry and Kendall (*J.*, 1951, 1723). In the present work the reactions were studied under carefully controlled experimental conditions and in the cases of (I; R = *cyclo*hexyl, *cyclo*hex-2-enyl, and allyl) the kinetics of the reactions were studied, thus permitting worthwhile discussion of the reaction mechanisms.

Table 1 summarises the yields of (I), (II), and (III) obtained on heating (I), containing differently constituted substituents R, for 48 hours at 200°. Since melts of the pure sulphides were used the initial concentrations of the reactants vary slightly, but without significance for the present purpose. Two reaction courses are obviously operative: (i) thermal isomerisation of (I) to (II), which is reversible when R = allyl, *trans*-but-2-enyl, and *cyclo*hex-2-enyl; and (ii) thermal decomposition of (I) to 2-mercaptobenzothiazole (III) and a hydrocarbon derived from R by the loss of hydrogen. As examples of (ii) may be cited (I; R = *cyclo*hexyl) which gives (III) and *cyclo*hexene, and (I; R = benzyl) which gives (III) and *trans*-stilbene [cf. Reed *et al.*, *loc. cit.*, who reported (II; R = benzyl) as the sole product of the iodine-catalysed pyrolysis of (I; R = benzyl) at 200°].



The relative importance of reactions (i) and (ii) and their absolute rates are seen to be critically dependent on the nature of R. An extreme case of the sole operation of (i) is found in (I; R = allyl) where no detectable amount of (III) is formed. An extreme case of the sole operation of (ii) is exemplified by (I; R = *cyclo*hexyl) where only a negligible amount (<0·2 mole %) of (II; R = *cyclo*hexyl) was found (see Experimental section). The relative facility of (ii) is seen to vary with the nature of R thus: primary alkyl < *sec.*-alkyl < aralkyl; and the change is also sensitive to slight structural changes in the alkenyl groupings thus: allyl < *trans*-but-2-enyl ≪ *cyclo*hex-2-enyl.

TABLE 1. *Thermal isomerisation and decomposition of* (I) (200° ± 2°, 48·0 *hours*).

[Yields: Mole % of (I), (II), and (III).]

Substituent R	Mole % (I)	Mole % (II)	Mole % (III)
Methyl	98	2	0·15
n-Octyl	96·5	0·9	~1
*iso*Propyl	83·5	2	13·0
*cyclo*Hexyl	90	0	7·7
Benzyl	~76	3·5	20·1
Allyl †	11	87	0
trans-But-2-enyl (20·0 hours)	55	41·5	2
,, (48·0 hours) *	28	65·5	3·7
,, (48·0 hours) §	32	63	3·7
*cyclo*Hex-2-enyl ‡	23·5	40·5	34·2

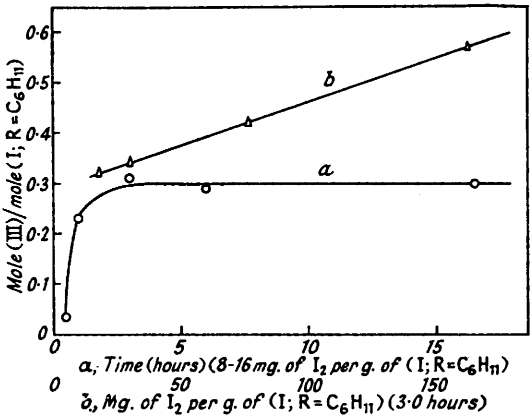
* Results of micro-scale experiment.
† Equilibrium mixture.
‡ Apparent equilibrium mixture.
§ Results of macro-scale experiment.

The reaction course of (I; R = *cyclo*hexyl) was uninfluenced by temperature within the range 200—230° and of (I; R = allyl) within the range 140—200°. In the case of (I) and (II) (R = *cyclo*hex-2-enyl), however, although at 110—140° the reversible isomerisation (i) suffered negligible contamination with (ii), at 200° (ii) intruded to a considerable extent. An unusual feature of the latter decomposition was that the volatile product originating from the *cyclo*hex-2-enyl grouping consisted mainly of benzene and *cyclo*hexene, the expected olefin, *cyclo*hexa-1 : 3-diene, being only a very minor constituent. A second unusual and unexplained feature of the 200° reaction is that an apparent equilibrium state is reached between the various products (see Experimental, Table 11).

The Iodine-Catalysed Decomposition of (I; R = cyclo*Hexyl*).—Contrary to its catalysis of the *isomerisation* of (I; R = Me and Et) to (II; R = Me and Et, respectively) (Reed *et al., loc. cit.*) iodine acts as an efficient catalyst for the *decomposition* of (I; R = *cyclo*hexyl) at 200° into (III) and *cyclo*hexene. Reaction conditions leading to the formation of ~30 mole % of (III) also yielded (II; R = *cyclo*hexyl) (4·6 mole %), a result in contrast with the absence of this product in the uncatalysed decomposition. The effects of reaction time and catalyst concentration on the yield of (III) are given in Fig. 1 and indicate (*a*) that for a constant initial iodine concentration (8—16 mg. of iodine per g. of sulphide) the yield of (III) reaches a maximum of ~30 mole %, and (*b*) that the yield of (III) after three hours' reaction is a linear function of the initial iodine concentration. The former result suggests that the catalyst is consumed during the reaction.

Reaction Kinetics.—The kinetics of the decomposition or reversible isomerisation have been investigated for (I; R = *cyclo*hexyl, allyl, and *cyclo*hex-2-enyl) under temperature conditions chosen to give a single reaction course, *i.e.*, the decomposition route (ii) for (I; R = *cyclo*hexyl) and the reversible isomerisation (i) for (I; R = allyl and *cyclo*hex-2-enyl).

FIG. 1.



The initial rates of 2-mercaptobenzothiazole formation from (I; R = *cyclo*hexyl) at 230° were measured at several concentrations, with diphenyl as an inert diluent. The first-order nature of the reaction is apparent from the linear initial rate–initial concentration relation. There were indications of deviation from the first-order law with increasing decomposition, possibly owing to the reversibility of the process or to environmental effects arising from the increasing accumulation of products. Rate constants determined for the decomposition of the pure sulphide in the temperature range 200—230° yielded a linear Arrhenius plot (E = 43·5 kcal. mole^{-1}).

The reversible isomerisations of (I) and (II) (R = allyl and *cyclo*hex-2-enyl) were studied quantitatively by an ultra-violet spectrometric method (see Experimental). The excellent linear plots which were obtained of $\log_{10}$ $[E^{1\%}_{1\,\mathrm{cm.}\,3265e} - E^{1\%}_{1\,\mathrm{cm.}\,3265t}]$ against time indicate that these isomerisations obey the kinetic law governing a reversible first-order reaction over an extensive range of reaction. Since the sum of the velocity constants for the forward (k_1) and reverse (k_2) reactions is obtainable from the slopes of the lines, and the ratio from the equilibrium concentrations of (II; R = allyl and *cyclo*hex-2-enyl), as estimated from the maximum $E^{1\%}_{1\,\mathrm{cm.}\,3265}$ values attained, k_1 and k_2 can readily be evaluated separately (Tables 2 and 3). The derived activation energies are given in Table 4.

TABLE 2. *Reversible isomerisation of* (I) *and* (II) (R = allyl).

Temp. (° K)	$10^6(k_1 + k_2)$ (sec.$^{-1}$)	Mole %		k_1/k_2	$10^6 k_1$ (sec.$^{-1}$)	$10^6 k_2$ (sec.$^{-1}$)
		$(I)_e$ *	$(II)_e$			
413 ± 0·1	2·78	6·9	93·1	13·5	2·59	0·19
433 ± 0·5	16·5	7·8	92·2	11·7	15·2	1·3
453 ± 0·5	82·1	9·2	90·8	9·9	74·4	7·7
473 ± 1·0	350	12·1	87·9	7·2	310	40

* Taken as 100 − mole % $(II)_e$.

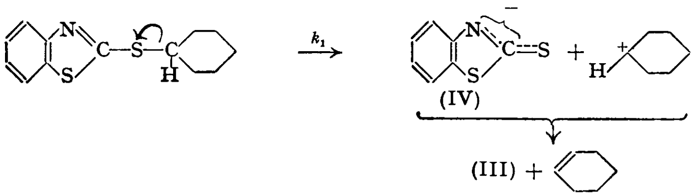
TABLE 3. *Reversible isomerisation of* (I) *and* (III) (R = *cyclo*hex-2-enyl).

Temp. (° K)	Initial concn. of (I) (mole l.$^{-1}$)	$10^6(k_1 + k_2)$ (sec.$^{-1}$)	Mole % (I)$_e$ *	Mole % (II)$_e$	k_1/k_2	10^6k_1 (sec.$^{-1}$)	10^6k_2 (sec.$^{-1}$)
383 ± 0·2	—	7·61	18·0	82·0	4·56	6·24	1·37
398 ± 0·2	—	33·4	21·4	78·6	3·67	26·2	7·2
413 ± 0·2	4·6	134	25·6	74·4	2·91	100	34
,,	0·36 †	65	45·6	54·4	1·19	35	30
,,	0·034 †	56	48·1	51·9	1·08	29	27

* Taken as 100 — mole % (II)$_e$. † *cyclo*Hexene as diluent.

The equilibrium proportions of (I) and (II) (R = allyl) were also determined with (II; R = allyl) as the initial reactant. The results (see Experimental, Table 12) confirm that the reaction is truly reversible.

Discussion of Reaction Mechanisms.—(1) *The mechanism of the decomposition reaction* (ii). The accumulated evidence suggests that the decomposition of (I) to (III) and (R–H) is ionic in nature. Thus, for (I; R = *cyclo*hexyl), we envisage:

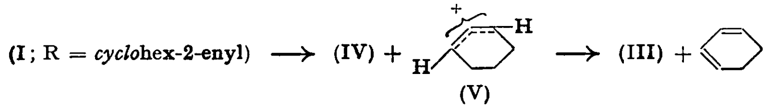


The rate-determining step is identified with a unimolecular heterolytic fission of the C–S bond to give the mesomeric thiobenzothiazolyl anion (IV) and the *cyclo*hexylcarbonium ion, being followed by a rapid proton-transfer reaction to give (III) and *cyclo*hexene. The reaction is thus analogous to *E*1 elimination processes (Hughes *et al.*, *J.*, 1948, 2038 *et seq.*).

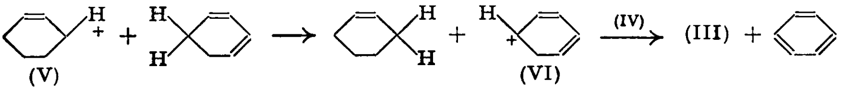
The formation of *trans*-stilbene from (I; R = benzyl) cannot be accounted for directly by a proton-transfer reaction between (IV) and a benzylcarbonium ion. However, it is possible that such a reaction occurs to yield the benzylidene diradical which is then stabilised by dimerisation to *trans*-stilbene (cf. Bickel and Waters, *Rec. Trav. chim.*, 1950, **69**, 312):

$$(\mathrm{I};\ \mathrm{R} = \text{benzyl}) \xrightarrow{k_1} (\mathrm{IV}) + \mathrm{C_6H_5{-}CH_2^+} \longrightarrow (\mathrm{III}) + \mathrm{C_6H_5{-}\dot{C}H} \xrightarrow[\text{Dimerisation}]{} \underset{trans}{\mathrm{C_6H_5{\cdot}CH = CH{\cdot}C_6H_5}}$$

The formation of *cyclo*hexene and benzene as the major products of the thermal decomposition of (I; R = *cyclo*hex-2-enyl) is in accord with the known behaviour of carbonium ions. The primary reactions are envisaged as:



the *cyclo*hexene and benzene then resulting from the interaction of the carbonium ion (V) with the *cyclo*hexa-1 : 3-diene (cf. Bartlett, Condon, and Schneider, *J. Amer. Chem. Soc.*, 1944, **66**, 1531; Schneider and Kennedy, *ibid.*, 1951, **73**, 5013, 5017, 5024):



The driving force of the reaction is the greater resonance stabilisation of (VI), containing the mesomeric pentadienyl-ion system $(\mathrm{R{\cdot}}\overbrace{\mathrm{CH{\cdots}CH{\cdots}CH{\cdots}CH{\cdots}CH}}^{+}\mathrm{{\cdot}R'})$, compared with the resonance stabilisation of the allyl ion system $(\mathrm{R{\cdot}}\overbrace{\mathrm{CH{\cdots}CH{\cdots}CH}}^{+}\mathrm{{\cdot}R'})$ present in (V).

The carbonium ions might be expected to cause some polymerisation of the olefinic products and in fact evidence for the formation of a hydrocarbon polymer was obtained. Additional support for the utilisation of some of the *cyclo*hexene in this way is provided by the preponderance of benzene in the isolated hydrocarbon mixture.

Two factors responsible for the relative facility of decomposition of (I), with different substituents R, can now be considered: (*a*) the rate of unimolecular heterolytic fission of the relevant C–S bond; and (*b*) the ease of removal of a proton from the derived carbonium ion. The first of these depends on the resonance stabilisation energy of the carbonium ion R^+ and is therefore expected to be facilitated by substitution as follows:

$$R^+_{\text{prim. alkyl}} < R^+_{sec.\text{-alkyl}} < R^+_{\text{aralkyl}} \sim R^+_{\text{alkenyl}}$$

This is the order observed experimentally for the ease of decomposition of (I) when this is the sole or major reaction. The intrusion of the second factor (*b*) becomes apparent when the relative rates of the decomposition (ii) and isomerisation (i) processes for a given compound are considered. The greater the ease of loss of a proton from R^+ the less will (i) compete with (ii). The extreme case of this is where $R^+ = C_6H_{11}{}^+$ and (ii) is the sole reaction; on the other hand the observed isomerisation of (I; R = Me) to (II; R = Me) as the predominant reaction is in agreement with the expected difficulty of removal of a proton from Me^+.

The catalytic action of iodine on the decomposition of (I; R = *cyclo*hexyl) is regarded as resulting from the formation of a sulphonium salt of the type $RR'SI^+\}I^-$, which increases the polarisation of the $S\text{–}C_{(cyclo\text{hexyl})}$ bond and consequently its ease of dissociation (see Tarbell and Harnish, *Chem. Reviews*, 1951, **49**, 1). Iodine-catalysis of the dehydration of alcohols has been similarly explained (Dhar *et al.*, *J.*, 1948, 2093).

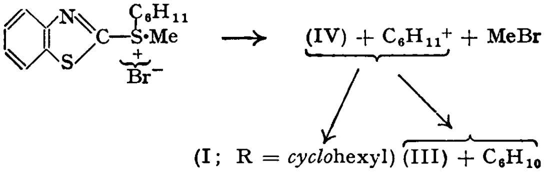
(2) *The mechanism of the isomerisation reaction* (ii). It is convenient to consider two groups of compounds separately: (*A*) (I; R = alkyl and aralkyl) and (*B*) (I; R = alkenyl).

(*A*) 2-*Alkyl- and* 2-*aralkyl-thiobenzothiazoles.* The isomerisation of these sulphides to the more thermally stable thiazoline derivatives (II; R = alkyl and aralkyl) is believed to proceed *via* the intermediate formation of the mesomeric thiobenzothiazolyl anion and the relevant carbonium ion, the rate-determining step again being the unimolecular heterolytic fission of the C–S bond. The isomerisation thus becomes an alternative to the decomposition reaction (ii), and is subject to the same governing factors (*a* and *b* above):

$$(\text{I}; \text{ R} = \text{alkyl or aralkyl}) \longrightarrow (\text{IV}) + R^+ \xrightarrow{\text{(ii)}} (\text{II}; \text{ R} = \text{alkyl or aralkyl})$$

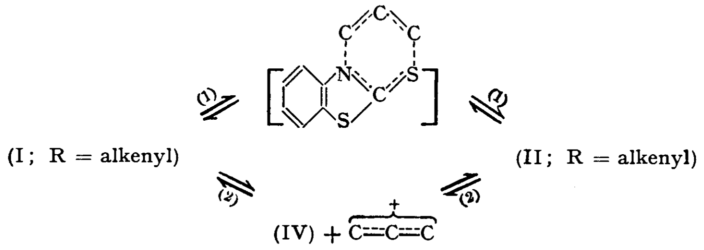
Iodine and bromine presumably catalyse these isomerisations (Reed *et al.*, *loc. cit.*) just as they do the decomposition of (I; R = *cyclo*hexyl) (see above), but the similar action of alkyl halides is not so clear.

It has now been found that when (I; R = Me) is heated with *cyclo*hexyl bromide at 200° methyl bromide is evolved and the following compounds are formed (in parentheses are given the yields in mole %): (III) (21); (I; R = Me) (~21); (I; R = *cyclo*hexyl) (~12); (II; R = Me) (~22); (II; R = *cyclo*hexyl) (~7). The formation of (II; R = Me or *cyclo*hexyl) is in agreement with Fry and Kendall's mechanism (*J.*, 1951, 1716) involving initial quaternisation of the nitrogen atom in (I) by the alkyl halide. On the other hand, the formation of (III) and (I; R = *cyclo*hexyl) in substantial amounts cannot be satisfactorily explained on this basis and it must be concluded that decomposition of an initially formed sulphonium salt is also operative (Davies and Sexton, *J.*, 1942, 304; Mann and Watson, *J. Org. Chem.*, 1948, **13**, 502):



(*B*) 2-*Alkenylthiobenzothiazoles.* The reversible thermal isomerisations of (I) and (II) (R = alkenyl) are analogous to the Claisen rearrangement of alkenyl aryl ethers to *o*-alkenylphenols and related rearrangements (see Tarbell, *Chem. Reviews*, 1940, **27**, 495; " Organic Reactions," Wiley, New York, 1944, Vol. II, p. 5).

Two unimolecular mechanisms are considered possible for the reversible isomerisations at present under discussion, *viz.*: (1) an intramolecular process involving a cyclic transition complex; and (2) an ionic process involving the formation of the mesomeric thiobenzothiazolyl and alkenyl ions:



Efforts to obtain evidence favouring one or other of these mechanisms were made for (I) and (II) (R = allyl and *cyclo*hex-2-enyl). In Table 4 are given the values for the Arrhenius energy of activation (*E*), the temperature-independent (*PZ*) factor, and the entropy of activation ($\Delta S^{\ddagger}$) for the isomerisation of the above compounds and for the decomposition of (I; R = *cyclo*hexyl). The $\Delta S^{\ddagger}$ values were derived from Eyring's equation for unimolecular gas-phase reactions (Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, 1941, p. 295), a value of unity being assumed for the transmission coefficient κ (cf. Shuler and Murphy, *J. Amer. Chem. Soc.*, 1950, **72**, 3155):

TABLE 4.

Reactant	*E* (kcal. mole^{-1})	*PZ* (sec.$^{-1}$)	$\Delta S^{\ddagger}$ (cal. deg.$^{-1}$ mole^{-1}) at 140° c
(I; R = allyl) †	31·3	$9{\cdot}6 \times 10^{10}$	−10·9
(II; R = allyl) †	34·6	$3{\cdot}9 \times 10^{11}$	−8·1
(I; R = *cyclo*hex-2-enyl) †	29·0	$2{\cdot}2 \times 10^{11}$	−9·2
(II; R = *cyclo*hex-2-enyl) †	33·5	$1{\cdot}8 \times 10^{13}$	−0·5
(I; R = *cyclo*hexyl) *	43·5	$6{\cdot}2 \times 10^{13}$	+1·9

* Data from $k_{\text{uni.}}$ at 200°. † Data from $k_{\text{uni.}}$ at 140°.

The large negative entropies of activation for the isomerisations of (I; R = allyl and *cyclo*hex-2-enyl) and (II; R = allyl) are consistent with the intramolecular mechanism (1). Similar interpretations have been given for the large negative entropies of activation observed for unimolecular Claisen rearrangements (Kincaid and Tarbell, *J. Amer. Chem. Soc.*, 1939, **61**, 3085; Murphy and Stein, *ibid.*, 1952, **74**, 1041; Shuler and Murphy, *loc. cit.*). For (II; R = *cyclo*hex-2-enyl) the *PZ* factor is normal and there is only a small negative entropy of activation; the significance of this result is obscure.

It could be argued that the rate-determining unimolecular heterolytic fission process (mechanism 2) may also be attended by a low *PZ* factor and thus a large negative entropy of activation, since the formation of the transition state may be accompanied by an increase of solvation. Such is the case for the Menschutkin reaction (Bell, *J.*, 1943, 629). However, in the decomposition of (I; R = *cyclo*hexyl) where the rate-determining step is undoubtedly a heterolytic fission of the C–S bond as required by mechanism (2), a normal *PZ* factor and a small positive entropy of activation are observed. It appears, therefore, that this dissociation does not involve any pronounced solvation of the ionic transition complex by the reactant or product molecules, and thus it may be inferred that the low *PZ* factors and large negative entropies of activation for the allyl-group isomerisations denote that mechanism (1) is operative.

The change in the reaction course of (I) and (II) (R = *cyclo*hex-2-enyl) when the temperature is increased from 140° to 200° is in keeping with intrusion of mechanism (2) at the higher temperature. Analogous decompositions, as alternatives to the normal rearrangement, have been observed with certain alkenyl aryl ethers (Tarbell, *locc. cit.*; Alexander and Kluiber, *J. Amer. Chem. Soc.*, 1951, **73**, 4304).

Further attempts to define the mechanism of the isomerisation of (I) and (II) (R = allyl and *cyclo*hex-2-enyl) were made by investigating the reaction of (I; R = *trans*-but-2-enyl). The isomerisation at 200° unexpectedly proved to be considerably slower than that of (I; R = allyl). Analysis of the non-equilibrated product after 20 hours at 200° indicated, directly or indirectly, the presence of the isomers listed in Table 5. The results suggest that both mechanisms (1) and (2) are operative in this case. Examination of models of the relevant molecules reveals that the formation of the cyclic transition state from (I; R = *trans*-but-2-enyl) necessary for the occurrence of (1) results in considerable steric interference between the terminal methyl group and the benzene ring. The intervention of mechanism (2) is thus favoured, with the formation of all three isomers of (II; R = but-2-enyl and 1-methylallyl)—the *trans*-but-2-enyl isomer being predominant in agreement with data from S_N1 substitutions and rearrangements in which the mesomeric methylallyl carbonium ion is an intermediate (Alexander, "Principles of Ionic Organic Reactions," Wiley, New York, 1950, Chapter 15; Catchpole and Hughes, *J.*, 1948, 4). No steric interference of the type considered above occurs with the other isomers or with (I) and (II) (R = allyl and *cyclo*hex-2-enyl) and therefore these may isomerise intramolecularly. The appearance of (II; R = 1-methylallyl) and the apparent absence of (I; R = 1-methylallyl) is understandable on the basis of the above reaction tendencies coupled with the expected higher velocity constant for the rearrangement of the latter isomer, as deduced from the analogous isomerisation of (I) and (II) (R = allyl). The slight intrusion of the decomposition reaction (ii), yielding (III) (see Table 1), is a consequence of the methylallyl carbonium ion being an intermediary in the reaction. The slowness of the isomerisations in this case, as compared with that of (I) and (II) (R = allyl), may be due to the higher *E* required for the operation of the ionic process. The *reduced* facility of isomerisation on passing from R = allyl to R = *trans*-but-2-enyl appears inexplicable in terms of a common reaction mechanism and hence lends support to the duality of mechanisms now proposed (Braude and Jones, *J.*, 1946, 122, 128; Tarbell and Wilson, *J. Amer. Chem. Soc.*, 1942, **64**, 607). The mechanism operating in the isomerisations of (I) and (II) (R = alkenyl) is seen to be critically dependent on the configurational nature of the alkenyl group. Similar effects have been observed in the thermal isomerisations of alkenyl thiocyanates (Mumm and Richter, *Ber.*, 1940, **73**, 843; Bergmann, *J.*, 1935, 1361).

TABLE 5. *Isomerisation of* (I; R = trans-*but-2-enyl*); 200° ± 1°; 20·0 *hours.*

<table>
<tr><th>R =</th><th><i>trans</i>-But-2-enyl</th><th><i>cis</i>-But-2-enyl</th><th>1-Methylallyl</th></tr>
<tr><td>(I), % of total</td><td>~85</td><td>~15</td><td>~0</td></tr>
<tr><td>(II), % of total</td><td colspan="2">(major) ~80—84 (minor)</td><td>~16—20</td></tr>
</table>

The ionic processes discussed above afford reasonable and self-consistent explanations of the varying characteristics of the isomerisations and decompositions of the molecular types (I) and (II). Direct evidence to refute the suggestion that free-radical intermediates might be involved (Fry and Kendall, *J.*, 1951, 1723) is obtained from experiments concerned with the behaviour of benzyl-type radicals under the decomposition conditions. On heating di(benzothiazol-2-yl) disulphide with dibenzyl at 200° or 230° a dehydrogenating reaction ensues which gives approximately 90% of the thiol (III), *trans*-stilbene, and a large amount of a dehydropolymer of dibenzyl. It follows from Part I that the dehydrogenating unit is the thiobenzothiazolyl radical, and therefore that the dehydropolymer represents a major molecular product of the *radical* $C_6H_5{\cdot}\dot{C}H{\cdot}CH_2{\cdot}C_6H_5$. This substance and dibenzyl were not detected in the decomposition of (I; R = benzyl), the liberated benzyl fragments appearing entirely as *trans*-stilbene (p. 4238). Again, when (I; R = *cyclo*hexyl) was heated in dibenzyl at 230°, (III) and *cyclo*hexene were the sole products. If *cyclo*hexyl and thiobenzothiazolyl radicals were intermediates, not only would radical attack on dibenzyl be expected to yield *trans*-stilbene and the dehydropolymer, but coupling of the *cyclo*hexyl radicals should also be evident (cf. Farmer and Moore, *J.*, 1951, 131).

EXPERIMENTAL

Ultra-violet light absorption measurements were made with absolute ethanol solutions by means of a Hilger Uvispek photoelectric spectrophotometer. Infra-red spectra were recorded by means of a Grubb-Parsons single-beam spectrometer.

Preparation of Materials.—2-*Methylthiobenzothiazole* (I; R = Me) had m. p. 49·5° (Found: C, 53·1; H, 4·0; N, 7·75; S, 35·2. Calc. for $C_8H_7NS_2$: C, 53·0; H, 3·9; N, 7·7; S, 35·35%). Light absorption: max., 2780, 2880, 2990 Å; ε, 12,800, 11,100, 8400 respectively].

3-Methyl-2-thiobenzothiazoline (II; R = Me) was prepared by the iodine-catalysed isomerisation of (I; R = Me) at 210—215° for 3 hours (Reed *et al.*, *loc. cit.*). It crystallised from ethanol in colourless prisms, m. p. 89·0—90·5° (Found: C, 53·05; H, 4·0; N, 7·65; S, 34·9%). Light absorption: max., 2300, 2410, 3240 Å; ε, 15,000, 15,600, 28,300 respectively.

2-iso*Propylthiobenzothiazole* (I; R = Pr^i) was prepared from the sodium derivative of 2-mercaptobenzothiazole and *iso*propyl bromide in refluxing ethanol (yield, 54·6%), b. p. 105—108°/<0·01 mm., n_D^{20} 1·6358 (Found: C, 57·4; H, 5·45; N, 6·75; S, 30·55. $C_{10}H_{11}NS_2$ requires C, 57·4; H, 5·3; N, 6·7; S, 30·6%). Light absorption: max., 2820, 2900, 3000 Å; $E^{1\%}_{1\,\text{cm.}}$, 585, 547, 456 respectively. Alkali-titration indicated the presence of *ca.* 0·4% of (III); $E^{1\%}_{1\,\text{cm.}\,3265}$ 12·8 indicated 0·45% of (II; R = Pr^i).

2-n-*Octylthiobenzothiazole* (I; R = n-C_8H_{17}), prepared as for (I; R = Pr^i), had b. p. 151—155°/<0·01mm., n_D^{20} 1·5873 (yield, 71·3%) (Found: C, 64·25; H, 7·75; N, 5·2; S, 23·0. $C_{15}H_{21}NS_2$ requires C, 64·5; H, 7·6; N, 5·0; S, 22·9%). Light absorption: max., 2815, 2900, 3010 Å; $E^{1\%}_{1\,\text{cm.}}$, 475, 434, 353 respectively. Alkali-titration indicated 0·4% of (III), and $E^{1\%}_{1\,\text{cm.}\,3265}$, 6·5 indicated the absence of (II; R = n-C_8H_{17}).

2-*cyclo*Hexylthiobenzothiazole (I; R = *cyclo*hexyl), prepared as for (I; R = Pr^i), crystallised from aqueous ethanol in needles, m. p. 47—48° (39%) (Found: C, 62·6; H, 6·1; N, 5·65, 5·8; S, 25·5. Calc. for $C_{13}H_{15}NS_2$: C, 62·6; H, 6·1; N, 5·6; S, 25·7%). Light absorption: max., 2810, 2890, 3000 Å; ε, 13,000, 12,200, 10,300, respectively. Ultra-violet analysis and alkali-titration showed the absence of (III) and (II; R = *cyclo*hexyl).

2-Benzylthiobenzothiazole (I; R = CH_2Ph), prepared as for (I; R = Pr^i) (yield, 99%), crystallised from aqueous ethanol in colourless prismatic plates, m. p. 39·5—40·5° (72%) (Found: C, 65·4; H, 4·5; N, 5·6, 5·75; S, 24·6. Calc. for $C_{14}H_{11}NS_2$: C, 65·35; H, 4·3; N, 5·45; S, 24·9%). Light absorption: max., 2810, 2890, 3000 Å; ε, 13,500, 12,700, 10,500 respectively. Ultra-violet analysis and alkali-titration showed the absence of (III) and (II; R = CH_2Ph).

2-*Allylthiobenzothiazole* (I; R = C_3H_5).—Allyl bromide (66·5 g., 0·55 mol.; b. p. 69·5—70°/750 mm., n_D^{20} 1·4695) was added to a stirred suspension of the sodium derivative of 2-mercaptobenzothiazole (III) (83·6 g., 0·5 mol.; NaOMe, 27 g., 0·5 mol.) in toluene, the mixture being heated at 80—90° for 7 hours. The product was poured into water, and the toluene layer separated and washed with 10% aqueous sodium hydroxide (2 × 150 ml.), followed by water, and finally dried ($CaCl_2$). Removal of solvent and distillation of the product gave the *thiazole* (I; R = C_3H_5), b. p. 126—129°/0·05 mm., n_D^{20} 1·6627 (71·4%) (Found: C, 58·0; H, 4·35; N, 6·95; S, 31·05. $C_{10}H_9NS_2$ requires C, 57·9; H, 4·4; N, 6·75; S, 30·95%). Light absorption: max., 2800, 2880, 3000 Å; $E^{1\%}_{1\,\text{cm.}}$, 609, 555, 444, respectively. The infra-red spectrum shows bands at 1636 and 920 cm.$^{-1}$, characteristic of the $R{\cdot}CH{=}CH_2$ grouping. The vibration at ~990 cm.$^{-1}$, also characteristic of this grouping, is masked by a strong skeletal vibration. Alkali-titration showed the absence of (III) and $E^{1\%}_{1\,\text{cm.}\,3265}$, 10·6 indicated 0·65% of (II; R = C_3H_5).

2-(trans-*But-2-enylthio*)*benzothiazole* (I; R = *trans*-$CH_3{\cdot}CH{:}CH{\cdot}CH_2$).—*trans*-But-2-en-1-ol, prepared by the reduction of *trans*-crotonaldehyde (b. p. 101·1—101·2°/742 mm., n_D^{20} 1·4370) with lithium aluminium hydride (Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197), had b. p. 120·9—121·2°/759 mm., n_D^{25} 1·4266. The infra-red spectrum showed that the $R{\cdot}CH{:}CH_2$ grouping was absent. *trans*-But-2-enyl chloride was prepared from the alcohol by Hatch and Nesbitt's method (*ibid.*, 1950, **72**, 727), and had b. p. 83·9—84·1°/759 mm., n_D^{20} 1·4353, n_D^{25} 1·4329. Infra-red analysis showed the presence of *ca.* 1% of 1-methylallyl chloride. The chloride (47·3 g., 0·523 mol.) was caused to react with the sodium derivative of (III) (83·6 g., 0·50 mol.; NaOMe, 27·0 g., 0·50 mol.) in ethanol (100 ml.) during 4 hours at 75—80°. The reactant concentrations were those conducive to S_N2 substitution (salt, ~2·9M; chloride, ~3·0M) (cf. Catchpole and Hughes, *J.*, 1948, 4). The crude product (98·8 g., 89%), on distillation, gave the pure *butenyl* compound (89·2 g., 81%), b. p. 110—115°/0·01—0·02 mm., which crystallised from aqueous ethanol in long colourless prisms, m. p. 42·0—42·5° (Found: C, 59·75; H, 4·95; N, 6·5; S, 28·8. $C_{11}H_{11}NS_2$ requires C, 59·7; H, 5·0; N, 6·3; S, 29·0%). Light absorption: max., 2810, 2890, 3000 Å; ε, 13,200, 12,300, 10,100, respectively. Alkali-titration showed the absence of (III) and ultra-violet analysis ($E^{1\%}_{1\,\text{cm.}\,3265}$, 3·0) indicated the absence of (II; R = CH_3·CH:CH·CH_2). The infra-red spectrum shows bands at 1667 and 961 cm.$^{-1}$ attributable to *trans*-R·CH:CH·R. Skeletal vibrations at 992 and 927 cm.$^{-1}$ (see below) will mask weak bands due to (I; R = 1-methylallyl); however, the absence of a band at ~1640 cm.$^{-1}$ indicates that this isomer is probably absent.

Mixture of 2-(trans-*But-2-enylthio)benzothiazole and* 2-(1-*Methylallylthio)benzothiazole*.—These were prepared as described for (I; R = *trans*-but-2-enyl) when a mixture of *trans*-but-2-enyl chloride and 1-methylallyl chloride (b. p. 64·0—83·9°/759 mm., n_D^{20} 1·4263 containing ~36% of the latter isomer, as based on the band at ~925 cm.$^{-1}$) was used. The mixed sulphides had b. p. 107—111°/0·005 mm. (Found: C, 59·65; H, 5·05; N, 6·4%). Light absorption: max., 2815, 2900, 3010 Å; $E^{1\%}_{1\,\text{cm.}\,2815}$, 592 and $E^{1\%}_{1\,\text{cm.}\,3265}$, 13·5, indicating 99·0% of (I) and 1·1% of (II). The infra-red spectrum was identical with that of pure (I; R = *trans*-CH_3·CH:CH·CH_2) except that a band occurred at 1636 cm.$^{-1}$, due to the R·CH:CH_2 grouping, absent in the latter. The similarity of the spectra of the mixture and pure (I; R = *trans*-CH_3·CH:CH·CH_2) in the 10-μ region suggests that both bands (at ~910, 990 cm.$^{-1}$) due to the C–H deformation of the R·CH:CH_2 grouping are masked by skeletal vibrations.

2-(cyclo*Hex-2-enylthio)benzothiazole* (I).—The preparation of this compound and its isomer (II) is described in Part I.

2-*Mercaptobenzothiazole* (III).—A pure sample, kindly supplied by Dr. D. S. P. Roebuck of Monsanto Chemicals Ltd. (Ruabon), had m. p. 178—179° (Found: C, 50·0; H, 3·15; N, 8·45; S, 38·2%; equiv., 166·1, 165·1. Calc. for $C_7H_5NS_2$: C, 50·3; H, 3·0; N, 8·4; S, 38·3%; equiv., 167·2). Light absorption: max., 3200 Å; ε, 23,400. Koch (*J.*, 1949, 401) gives max., 3250 Å and ε, 27,500, and Morton and Stubbs (*J.*, 1939, 1321) gives max., 3250 Å, ε, 27,000. The value of 3200 Å, obtained by photoelectric spectrometry, was checked with another sample of (III). The photographic method gave, for the above sample, max., 3210 Å, ε, 24,000, so that it must be concluded that the results of Morton and Stubbs (*loc. cit.*) and Koch (*loc. cit.*) are in error.

Thermal isomerisations and decompositions.

General Analytical Procedure.—Weighed samples of the compounds were heated *in vacuo* in a thermostatically controlled oil-bath for the appropriate time. Estimation of (III) was made by titration of an ethanolic solution of the product with standard sodium hydroxide (phenolphthalein) or by the alkali-extraction procedure described in Part I. Isomerisations of (I) and (II) were followed by measuring the change in the ultra-violet light absorption properties. (I) exhibits intense absorption in the region 2800—3000 Å, which is resolved into three maxima at about 2810, 2890, and 3000 Å (the exact positions depending on the nature of R), and has negligible absorption in the region of 3250 Å (cf. Morton and Stubbs, *loc. cit.*). (II) has maxima at about 2400 and 3260 Å and a minimum at about 2800 Å (Morton and Stubbs, *loc. cit.*). (II) was thus estimated by measuring the intensity of absorption at 3265 Å, allowance being made for the absorption of (III) (if present) which also exhibits high-intensity absorption at this wave-length. The concentration of (I) was obtained by difference and checked by measuring the absorption intensity of the mixture at 2815 Å. The absorption intensities for pure (I), (II), and (III) at 2815 and 3265 Å are recorded in Table 6.

TABLE 6. *Ultra-violet spectroscopic data for* (I) *and* (II) (*in ethanol*).

	(I)		(II)	
R	$E^{1\%}_{1\,\text{cm.}\,2815}$	$E^{1\%}_{1\,\text{cm.}\,3265}$	$E^{1\%}_{1\,\text{cm.}\,2815}$	$E^{1\%}_{1\,\text{cm.}\,3265}$
Methyl	693	2·2	147·9	1505
*iso*Propyl	590	~2	105·0 *	1250 *
n-Octyl	476	~2	78·0 *	931 *
*cyclo*Hexyl	522	2·0	86·0	1046
*cyclo*Hex-2-enyl	548·3	~2	88·8	1058
Benzyl	526	4·3	81·6	1000
Allyl	610	~2	108·5	1317
trans-But-2-enyl	597	3·0	104·1	1218
Hydrogen (III)	—	—	170·5	1238

* Based on values for (II; R = *cyclo*hex-2-enyl).

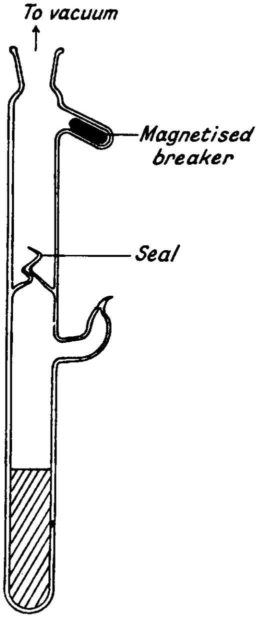
Thermal Isomerisations and Decompositions.—(1) The sulphide (I; R = Me), when heated at 200° ± 2° for 48·0 hours, gave a product containing unchanged (I; R = Me) (98%), (II; R = Me) (2·0%), and (III) (0·13%) (Light absorption: $E^{1\%}_{1\,\text{cm.}\,2815}$, 682; $E^{1\%}_{1\,\text{cm.}\,3265}$, 31·1).

(2) The sulphide (I; R = Pr^i) (3·73 g.), heated at 200° ± 2° for 48·0 hours, gave (III) (0·386 g., 0·130 mol.) and an alkali-insoluble product (3·19 g.), n_D^{20} 1·6371, consisting of (I; R = Pr^i) (97·5%) and (II; R = Pr^i) (2·5%) (Found: C, 57·4; H, 5·3; N, 6·7%. Light absorption: $E^{1\%}_{1\,\text{cm.}\,2815}$, 575·7; $E^{1\%}_{1\,\text{cm.}\,3265}$, 34·1).

(3) The sulphide (I; R = n-C_8H_{17}) (8·57 g.), on being heated at 200° ± 1° for 48·0 hours, gave (III) (0·085 g.) and an alkali-insoluble product (8·35 g.) consisting of (I) (99%) and (II) (R = n-C_8H_{17}) (~0·9%) (Found: C, 64·4; H, 7·6; N, 4·9; S, 22·7, 22·85%. Light absorption: $E^{1\%}_{1\,\text{cm.}\,2815}$, 472·3; $E^{1\%}_{1\,\text{cm.}\,3265}$, 10·0). A second sample of the sulphide, heated as above, but from which (III) had not been removed, contained ~0·9% of the latter (Light absorption: $E^{1\%}_{1\,\text{cm.}\,2815}$, 472·9; $E^{1\%}_{1\,\text{cm.}\,3265}$, 21·0).

(4) (I; R = *cyclo*Hexyl). (*a*) The sulphide (5·94 g.) was heated at 200° ± 2° for 72·4 hours in the apparatus shown in Fig. 2. This was connected to a weighed receiver, the assembly was evacuated and isolated from the line, and after breakage of the seal the volatile products were transferred to the receiver by cooling of the latter in liquid air. A second evaporative distillation of the volatile product (0·195 g.) gave almost pure *cyclo*hexene (0·192 g.), n_D^{20} 1·4473 (Found: C, 87·2; H, 12·2; S, 0·3. Calc. for C_6H_{10}: C, 87·7; H, 12·3%). The infra-red spectrum of this sample was identical with that of pure *cyclo*hexene. The non-volatile product consisted of (III) (0·443 g., 0·111 mol.), m. p. 176—178°, mixed m. p. 178—179°, which after crystallisation from water had m. p. and mixed m. p. 178—179°, and an alkali-insoluble product (5·21 g.), m. p. and mixed m. p. with (I; R = *cyclo*hexyl) 45—48°, containing (I) (98·9%) and (II; R = *cyclo*hexyl) (0·25%) (Found: C, 62·8; H, 6·0; N, 5·8%. Light absorption: $E^{1\%}_{1\,\text{cm.}\,2815}$, 515·7; $E^{1\%}_{1\,\text{cm.}\,3265}$, 4·5).

FIG. 2.



(*b*) The sulphide (4·956 g.), when heated at 200° ± 2° for 48·0 hours and worked up in the usual way, gave (III) (0·255 g., 0·077 mol.) and unchanged sulphide (4·48 g.), m. p. and mixed m. p. 46·5°.

(*c*) Heating the sulphide (6·110 g.) at 230° ± 1° for 5·0 hours and working up the product as in (*a*) gave: (i) slightly impure *cyclo*hexene [0·217 g., 92·5% based on yield of (III)], n_D^{20} 1·4477 (Found: C, 87·1; H, 12·1; S, 0·5%), the infra-red spectrum of which was identical with that of pure *cyclo*hexene; (ii) (III) (0·478 g., 0·117 mol.); and (iii) a mixture of (I) (~100%) and (II; R = *cyclo*hexyl) (~0·15%) (Light absorption: $E^{1\%}_{1\,\text{cm.}\,2815}$, 527; $E^{1\%}_{1\,\text{cm.}\,3265}$, 3·6).

(*d*) *Iodine-catalysed decomposition.* The sulphide (3·038 g.) and iodine (46·3 mg., equiv. to 15·24 mg. per g. of sulphide) were heated at 200° ± 1° for 6·0 hours in the apparatus shown in Fig. 2. The products consisted of: (i) slightly impure *cyclo*hexene (0·180 g.), b. p. 82·5°, n_D^{20} 1·4500 (Found: C, 86·1; H, 11·8%), identified by its infra-red spectrum; (ii) (III) (0·613 g., 0·302 mol.), m. p. and mixed m. p. 178—179° (Found: equiv., 167·5. Calc. for $C_7H_5NS_2$: equiv., 167·2); (iii) unchanged sulphide (1·90 g.), m. p. 43—46°, which after crystallisation from aqueous ethanol had m. p. and mixed m. p. 47—48°; and (iv) 3-cyclo*hexyl-2-thiobenzothiazoline* (II; R = *cyclo*hexyl) (0·14 g.), m. p. 97—100°, which was separated from (iii) by virtue of its insolubility in concentrated hydrochloric acid (cf. Reed *et al.*, *loc. cit.*). On crystallisation from ethanol pure (II; R = *cyclo*hexyl) was obtained as light yellow prismatic needles, m. p. 104—105° (Found: C, 62·6; H, 6·2; N, 5·55; S, 25·4. $C_{13}H_{15}NS_2$ requires C, 62·6; H, 6·1; N, 5·6; S, 25·7%). Light absorption: max., 2420, 3280 Å; ε, 13,700, 26,000, respectively).

(*e*) In an experiment similar to (*d*) the sulphide (3·004 g.), heated with iodine (44·7 mg., 14·9 mg. per g. of sulphide) at 200° ± 1° for 18·1 hours, gave: (i) impure *cyclo*hexene (0·223 g.), n_D^{23} 1·4516; (ii) (III) (0·597 g., 0·296 mol.); (iii) unchanged sulphide (1·60 g.); and (iv) (II; R = *cyclo*hexyl) (0·4 g.), m. p. 103—105°.

(*f*) *Decomposition in dibenzyl solution.* Heating a mixture of the sulphide (3·00 g.) and dibenzyl (3·00 g.) at 230° ± 1° for 8·0 hours gave (III) (0·369 g., 0·183 mol.) and an alkali-insoluble product which was separated, by trituration with concentrated hydrochloric acid, into the unchanged sulphide (2·38 g.), m. p. and mixed m. p. 46—47°, and dibenzyl (2·95 g.) containing ~0·5% of *trans*-stilbene (Light absorption: max., 2540, 2590, 2650, 2690, 2950 Å; $E^{1\%}_{1\,\text{cm.}\,2590}$, 26·16; $E^{1\%}_{1\,\text{cm.}\,2950}$, 7·64). The original dibenzyl contained ~0·4% of *trans*-stilbene (Light absorption: max., 2540, 2590, 2650, 2690 Å; $E^{1\%}_{1\,\text{cm.}\,2590}$, 26·14; $E^{1\%}_{1\,\text{cm.}\,2950}$, 6·04].

(5) The sulphide (I; R = CH_2Ph) (4·017 g.), after 48·0 hours at 200° ± 2°, gave (III) (0·525 g., 0·201 mol.) and an alkali-insoluble product (3·30 g.). The latter partly dissolved in warm light petroleum (b. p. 40—60°), leaving (II; R = CH_2Ph) (0·14 g.) which crystallised from ethanol in light yellow needles, m. p. 150·0—150·5° (Reed *et al.*, *loc. cit.*, give m. p. 149—150°) (Found: C, 65·35; H, 4·6; N, 5·4; S, 24·5%). Light absorption: max., 2410, 3260 Å; ε, 12,900, 25,800 respectively. Chromatographic separation of the petroleum solution (200 ml.) on alumina (90 g.) by elution with successive 100-ml. portions of benzene–light petroleum (1 : 1 by vol.) gave: (i) a light yellow solid (0·85 g.); (ii) unchanged (I; R = CH_2Ph) (1·58 g.), m. p. 39—40·5°, mixed m. p. 40—41°; and (iii) slightly impure (ii) (0·30 g.), m. p. 37—39°, mixed m. p. 38—41°. Fraction (i), in light petroleum (b. p. 40—60°) (100 ml.), was rechromatographed on alumina (20 g.) and developed with the same solvent to give the following fractions (volumes in parentheses refer to eluate): (i*a*) (135 ml.), slightly impure *trans*-stilbene (0·10 g.), m. p. 112—123, which on crystallisation from aqueous ethanol gave the pure compound (0·06 g.), m. p. and mixed m. p. 124—124·5° (Found: C, 93·1; H, 6·65. Calc. for $C_{14}H_{12}$: C, 93·3; H, 6·7%). Light absorption: max., 2950 Å, ε, 29,800; (i*b*) (25 ml.), impure *trans*-stilbene (0·05 g.) which was added to the mother-liquor from (i*a*) and recrystallised, to give almost pure *trans*-stilbene (0·05 g.), m. p. 121—124·5°, mixed m. p. 122—124·5°; (i*c*) (20 ml.), a mixture of *trans*-stilbene and sulphide (0·03 g.); and (i*d*) (column stripped with benzene), unchanged (I; R = CH_2Ph) (0·50 g.), m. p. and mixed m. p., 39—40°.

(6) (*a*) The sulphide (I; R = allyl) (14·72 g.) was heated at 200° ± 1° for 3·0 hours. Alkali-extraction of the product in chloroform showed the absence of (III). Trituration of the alkali-insoluble product (13·98 g.) with concentrated hydrochloric acid gave the *thiazoline* (II; R = allyl) (12·39 g.), m. p. 65—67°, which crystallised from aqueous ethanol (charcoal) in colourless plates, m. p. 67·5—68·5° (Found: C, 57·85; H, 4·45; N, 6·7; S, 30·6. $C_{10}H_9NS_2$ requires C, 57·9; H, 4·4; N, 6·75; S, 30·95%). Light absorption: max., 2400, 3240 Å; ε, 13,840, 27,360 respectively. The infra-red spectrum shows bands at 1641 and 924 cm.$^{-1}$ attributable to the $R{\cdot}CH{:}CH_2$ grouping.

(*b*) By heating the sulphide (4·67 g.) at 200° ± 2° for 48·0 hours in the apparatus described in Fig. 2 it was shown that no volatile products were formed and that (III) was again absent. The product (4·48 g.) gave (II; R = allyl) (3·94 g.), m. p. 67·0—67·5°, on trituration with concentrated hydrochloric acid.

(7) (*a*) The sulphide (I; R = *trans*-but-2-enyl) (10·02 g.), heated at 200° ± 1° for 20·0 hours, gave (III) (0·147 g., 0·0194 mol.), m. p. and mixed m. p. 177—179°, and an alkali-insoluble product (9·85 g.) separable by trituration with concentrated hydrochloric acid into (i) an insoluble product (2·87 g.), m. p. 62—73°, and (ii) a soluble product (5·98 g.) regenerated by neutralisation of the acid. (i) consisted of (II; R = x-methylallyl) (96·5%) (Found: C, 59·9; H, 5·2; N, 6·35; S, 28·7%). Light absorption: $E^{1\%}_{1\,\text{cm.}\,2815}$, 103·6; $E^{1\%}_{1\,\text{cm.}\,3265}$, 1174. The infra-red spectrum shows bands at 965 cm.$^{-1}$, due to *trans*-$CHR{:}CHR$, and at 1635 and 924 cm.$^{-1}$, due to $R{\cdot}CH{:}CH_2$. The intensities of the bands at 1635 and 924 cm.$^{-1}$ indicate the presence of 16—20% of (II; R = 1-methylallyl). Crystallisation of (i) from aqueous ethanol gave an apparently pure sample of the *thiazoline* (II; R = *trans*-but-2-enyl) as colourless needles, m. p. 77·5—78·5° (Found: C, 59·5; H, 5·0; N, 6·25; S, 28·65, 29·0%). Light absorption: max., 2410, 3260 Å; ε, 15,000, 27,300 respectively. The infra-red spectrum of this compound shows a strong band at 965 cm.$^{-1}$ indicating the *trans*-$CHR{:}CHR$ grouping; the absence of a band at 1635 cm.$^{-1}$ suggests the absence of (II; R = 1-methylallyl). (ii), a partly crystallising light-orange oil, was a mixture of (I; R = x-methylallyl) (91·4%) and (II; R = x-methylallyl) (3·9%) (Found: C, 59·45; H, 5·15; N, 6·35, 6·4%). Light absorption: max., 2810, 2890, 3000 Å; $E^{1\%}_{1\,\text{cm.}\,2815}$, 549·5; $E^{1\%}_{1\,\text{cm.}\,3265}$, 47·4. The infra-red spectrum of (ii) is similar to, but not identical with, that for pure (I; R = *trans*-but-2-enyl). Since the latter compound has a skeletal vibration at 927 cm.$^{-1}$ the presence of a band in this position cannot be used as diagnostic evidence for (I; R = 1-methylallyl). However, the absence of a band at ~1640 cm.$^{-1}$ strongly suggests the absence of this compound. Absorption in the region of 670 cm.$^{-1}$ is only slightly greater than that for pure (I; R = *trans*-but-2-enyl), making it difficult to establish the presence of the *cis*-$CHR{:}CHR'$ grouping (however, see below). The intensity of the 965 cm.$^{-1}$ band shows that ~85% of (I; R = *trans*-but-2-enyl) is present.

Distillation of a portion (4·45 g.) of (ii) gave (ii*a*), b. p. 118—120°/0·04 mm. (3·80 g.), containing (I) (96·5%) and (II; R = x-methylallyl) (~1·7%) (Found: C, 59·6; H, 5·0; N, 6·4; S, 28·6%. Light absorption: max., 2815, 2900, 3010 Å; $E^{1\%}_{1\,\text{cm.}\,2815}$, 578; $E^{1\%}_{1\,\text{cm.}\,3265}$, 21·4). The infra-red spectrum of this sample is very similar to that of (ii), except that the band intensity at 1674 cm.$^{-1}$ in the latter is greatly reduced and the band centre now appears at 1667 cm.$^{-1}$

(region for *cis*- and *trans*-CHR:CHR); there is no band in the 1640 cm.$^{-1}$ region. (ii*a*) partly crystallised and filtration of a portion (2·65 g.) gave pure (I; R = *trans*-but-2-enyl) (0·85 g.), m. p. and mixed m. p., 42·0—42·5°. The filtrate (1·66 g.) contained (I) (96·6%) and (II; R = x-methylallyl) (2·4%) (Light absorption: max., 2820, 2900, 3010 Å; $E^{1\%}_{1\,\mathrm{cm.}\,2815}$, 579; $E^{1\%}_{1\,\mathrm{cm.}\,3265}$, 29·1). The infra-red spectrum of the filtrate is very similar to that of (ii) and (ii*a*) except that the band at ~1664 cm.$^{-1}$ is intensified slightly. There is no band at ~1640 cm.$^{-1}$ due to the R·CH:CH$_2$ grouping. Absorption in the region of 670 cm.$^{-1}$, not present in pure (I; R = *trans*-but-2-enyl), may be due to the *cis*-CHR:CHR grouping. The intensity of the band at 965 cm.$^{-1}$ shows that ~60% of *trans*-CHR:CHR is present.

(*b*) Heating the sulphide (10·11 g.) for 48·0 hours at 200° ± 0·5° gave (III) (0·280 g., 0·0367 mol.) and a mixture (9·53 g.) of (I) (33·7%) and (II; R = x-methylallyl) (66·5%). Light absorption: $E^{1\%}_{1\,\mathrm{cm.}\,2815}$, 270·4; $E^{1\%}_{1\,\mathrm{cm.}\,3265}$, 810.

(8) The thiazoline (II; R = *cyclo*hex-2-enyl) (5·07 g.) was heated at 200° ± 2° for 48·0 hours in the apparatus described in Fig. 2. Evaporative distillation of the product yielded a colourless liquid (0·374 g.), n_D^{20} 1·4795—1·4805 (Found: C, 89·7; H, 9·6; S, 0·45%; C : H = 6 : 7·67). The infra-red spectrum reveals the presence of *cyclo*hexene (~35%), benzene (~65%), and a third component. The ultra-violet spectrum (max., 2430, 2485, 2545, 2605 Å; $E^{1\%}_{1\,\mathrm{cm.}}$, 23·5, 32·0, 37·0, 31·8 respectively) confirms the presence of benzene (max., 2430, 2485, 2545, 2605 Å; $E^{1\%}_{1\,\mathrm{cm.}}$, 10·5, 19·5, 23·1, 15·6 respectively) and, taken in conjunction with the infra-red spectral data, indicates the presence of a compound having intense absorption in the region of 2400—2700 Å. This is assumed to be *cyclo*hexa-1 : 3-diene (Henri and Pickett, *J. Chem. Phys.*, 1939, **7**, 439, give max., 2475, 2560, 2650 Å; ε, 5400, 7900, 6000 respectively). From the intensities of absorption at 2545 and 2580 Å ($E^{1\%}_{1\,\mathrm{cm.}\,2580}$ 26·3) it is calculated that the mixture contains 2·4% of the diene ($E^{1\%}_{1\,\mathrm{cm.}\,2545,\,2580}$, 906) and 69% of benzene ($E^{1\%}_{1\,\mathrm{cm.}\,2580}$, 6·6), the light absorption of *cyclo*hexene at these wave-lengths being assumed to be negligible.

Working up the non-volatile product in the usual way gave (III) (1·340 g., 0·391 mol.) and a mixture (3·17 g.) of (I) (27·2%), (II; R = *cyclo*hex-2-enyl) (60·1%), and unidentified polymeric hydrocarbon (~13%) (Found: C, 64·2; H, 5·65; N, 5·5; S, 24·1, 24·4. Calc. for $C_{13}H_{13}NS_2$: C, 63·1; H, 5·3; N, 5·7; S, 25·9%). Light absorption: $E^{1\%}_{1\,\mathrm{cm.}\,2815}$, 202·7; $E^{1\%}_{1\,\mathrm{cm.}\,3265}$, 635·6.

(9) The sulphide (I; R = *cyclo*hex-2-enyl) (3·52 g.), heated at 200° ± 2° for 48·0 hours, gave (III) (0·744 g., 0·313 mol.), m. p. and mixed m. p. 178·5°, and a mixture (2·51 g.) of (I) and (II; R = *cyclo*hex-2-enyl) and polymeric hydrocarbon (see Table 11).

Kinetic Data.—The initial rates of decomposition of (I; R = *cyclo*hexyl) were obtained by estimating (III) by the alkalimetric method. The data are summarised in Tables 7 and 8.

TABLE 7. *Decomposition of* (I; R = cyclo*hexyl*).

Temp. (° K)	[I] (mole l.$^{-1}$)	r_t (mole l.$^{-1}$ hr.$^{-1}$)	$10^7 k_{\mathrm{uni.}}$ (sec.$^{-1}$)
473° ± 1°	4·24	0·0075	4·9
488° ± 0·5°	4·20	0·032	21
503° ± 1°	4·14	0·115	77·$_6$
,,	1·89 *	0·052	—
,,	0·90 *	0·024$_5$	—
,,	1·83 †	0·047	—

* Diphenyl as diluent. † Dibenzyl as diluent.

TABLE 8. *Decomposition of* (I; R = cyclo*hexyl*) *at* 200° ± 2°.

Time (hours)	12·0	18·0	24·25	36·2	48·0 *	96·0	144·0 †	263·0
Mole % of (III)	2·42	3·38	4·26	6·4	8·3	14·8	19·7	27·3
$10^7 k_{\mathrm{uni.}}$ (sec.$^{-1}$)	5·7	5·3	5·0	5·1	5·0	4·6	4·2	3·4

* Product contains (I) (90·7 mole %) and no (II; R = *cyclo*hexyl). Light absorption: $E^{1\%}_{1\,\mathrm{cm.}\,2815}$, 496·2; $E^{1\%}_{1\,\mathrm{cm.}\,3265}$, 72·1.

† Product contains (I) (79·1 mole %) and (II; R = *cyclo*hexyl) (0·8 mole %). Light absorption: $E^{1\%}_{1\,\mathrm{cm.}\,2815}$, 465·7; $E^{1\%}_{1\,\mathrm{cm.}\,3265}$, 185·2.

The data for the reversible isomerisations of (I) and (II) (R = allyl, *trans*-but-2-enyl, and *cyclo*hex-2-enyl) and for the combined isomerisation and decomposition of (I) and (II) (R = *cyclo*hex-2-enyl) are summarised in Tables 9—13. The kinetic law for a reversible first-order reaction, $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$, is given by equation (i):

$$\ln x_e/(x_e - x_t) = (k_1 + k_2)t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

where x_t = concentration of A converted into B at time t and x_e = concentration of A converted into B at equilibrium, the initial concentration of B being zero. Thus for the above

TABLE 9. *Reversible isomerisation of* (I) *and* (II) (R = cyclo*hex-2-enyl*) (4·6 *mole l.*$^{-1}$) *at* 140° ± 0·2°.

Time (hrs.)	$E^{1\%}_{1\,\text{cm.}\,2815}$	$E^{1\%}_{1\,\text{cm.}\,3265}$	Mole % of (III)	Mole % of (I)	Mole % of (II)	Total mole %
		(I; R = cyclo*Hex-2-enyl.*)				
0	522·3	61·0	0	94·4	5·6	100·0
0·5	458·5	207·4	—	80·5	19·6	100·1
0·75	434·2	267·9	—	75·1	25·3	100·4
1·0	410·1	327·3	—	69·8	30·9	100·7
1·5	367·3	424·2	—	60·5	40·1	100·6
2·0	336·8	504·8	—	53·7	47·7	101·4
2·5	304·6	566·7	—	46·9	53·6	100·5
3·0	283·4	619·1	—	42·2	58·5	100·7
4·5	239·8	705·5	—	32·9	66·7	99·6
6·0	222·5	750·7	—	29·1	70·9	100·0
12·0	209·5	787·0	0·97	26·0	73·4 *	100·4
24·0	207·2	784·3	1·47	25·6	72·6	99·7
48·0	208·5	782·7	2·25	25·7	71·7	99·7
96·0	211·8	785·2	3·44	26·0	70·7	100·1
		(II; R = cyclo*Hex-2-enyl.*)				
48·0	201·9	801·7	1·22	24·3	74·6	100·1
96·0	202·0	807·0	2·49	24·3	73·7	100·5

* 74·4 mole % on basis of absence of (III).

TABLE 10. *Reversible isomerisation of* (I) *and* (II) (R = cyclo*hex-2-enyl*).

(i) *At* 110·0° ± 0·2°.

Time (hrs.)	0	3·0	6·0	8·0	10·5	13·0	16·0	20·5	24·0	30·0	144·0	192·0
$E^{1\%}_{1\,\text{cm.}\,3265}$	61·0	126·0	179·5	218·6	259·3	299·3	346·6	407·3	449·6	526·4	867·5	867·0
Mole % of (II)	5·6	11·9	17·0	20·7	24·6	28·3	32·8	38·5	42·5	49·8	82·0	82·0

(ii) *At* 125·0° ± 0·2°.

Time (hrs.)	0	1·0	2·0	3·0	4·1	5·0	6·0	8·0	48·0	96·25	144·0
$E^{1\%}_{1\,\text{cm.}\,3265}$	61·0	144·2	223·8	288·6	355·8	405·8	456·8	543·7	822·0	834·2	827·7
Mole % of (II)	5·6	13·6	21·2	27·3	34·0	38·4	43·2	51·4	77·7	78·9	78·3

(iii) *In* cyclo*hexene*; [I] 0·36 *mole l.*$^{-1}$; *at* 140·0° ± 0·2°.

Time (hrs.)	0	1·5	3·0	4·5	6·0	24·0	48·0 *
$E^{1\%}_{1\,\text{cm.}\,3265}$	52·8	209·6	318·1	392·7	448·2	574·0	575·5
Mole % of (II) †	4·8	19·8	30·1	37·1	42·4	54·3	54·4

(iv) *In* cyclo*hexene*; [I] 0·0344 *mole l.*$^{-1}$; *at* 140·0° ± 0·2°.

Time (hrs.)	0	1·5	3·0	4·5	6·0	7·5	24·0	48·0	72·0	96·0
$E^{1\%}_{1\,\text{cm.}\,3265}$	52·8	162·5	262·5	341·7	395·0	437·5	539·2	545·9	550·0	546·9
Mole % of (II) †	4·8	15·4	24·8	32·3	37·3	41·4	51·0	51·6	52·0	51·7

* Estimation of (III) indicates 3·2 mole % of (III) and 51·2 mole % (II).
† Assumed (III) is absent.

TABLE 11. *Thermal isomerisation and decomposition of* (I) *and* (II) (R = cyclo*hex-2-enyl*) *at* 200° ± 1°.

(i) (I; R = cyclo*Hex-2-enyl*).†

Time (hrs.)	1·0	3·0	6·0	10·0	24·0	48·0
$E^{1\%}_{1\,\text{cm.}\,2815}$	288·0	273·0	261·3	244·4	230·1	228·3
$E^{1\%}_{1\,\text{cm.}\,3265}$	648·0	706·5	739·8	763·0	798·3	801·3
Mole % of (III)	13·3	24·7	28·6	29·9	32·4	34·2
Mole % of (I)	39·6	33·7	30·6	27·3	24·0	23·3
Mole % of (II)	48·1	41·9	40·7	41·4	41·9	40·3
Total mole %	101·0	100·3	99·9	98·6	98·3	97·8

(ii) (II; R =cyclo*Hex-2-enyl*).

Time (hrs.)	1·0	3·0	6·0	10·0	24·0	48·0
$E^{1\%}_{1\,\text{cm.}\,2815}$	288·5	264·9	251·1	250·4	233·0	227·0
$E^{1\%}_{1\,\text{cm.}\,3265}$	665·4	750·6	770·2	789·5	800·7	820·6
Mole % of (III)	13·0	24·8	30·5	33·9	33·8	37·3
Mole % of (I)	39·8	31·8	28·1	27·1	24·1	22·3
Mole % of (II)	50·0	45·6	41·5	39·6	40·6	38·9
Total mole %	102·6	102·2	100·1	100·6	98·5	98·5

† Original sample had $E^{1\%}_{1\,\text{cm.}\,2815}$, 522·3; $E^{1\%}_{1\,\text{cm.}\,3265}$, 61·0.

TABLE 12. *Reversible isomerisation of* (I *and* II; R = *allyl*).

(I; R = Allyl):

(i) *At* 140° ± 0·1°; [I] 5·45 mole l.$^{-1}$.

Time (hrs.) ...	12·0	24·0	36·0	48·1	60·0	72·0	96·0	120·0	144·0	168·0	336·0	504·0	672·0
$E^{1\%}_{1\,\text{cm.}\,3265}$ ...	131·0	261·5	361·1	464·2	550·3	633·8	744·5	882·5	954·0	1035	1206	1223	1229
Mole % of (II)	10·0	19·9	27·4	35·3	42·1	48·1	56·5	67·0	72·4	78·6	91·6	92·9	93·3

(ii) *At* 160° ± 0·1°; [I] 5·4 *mole l.*$^{-1}$.

Time (hrs.) ...	2·0	4·0	6·0	8·0	12·0	16·0	20·0	24·0	48·0	96·0	144·0
$E^{1\%}_{1\,\text{cm.}\,3265}$ ...	140·3	252·8	359·7	454·1	618·3	749·3	852·6	953·7	1164	1213	1210
Mole % of (II)	10·7	19·2	27·3	34·5	47·0	56·8	64·7	72·4	88·4	92·2	91·9

(iii) *At* 180° ± 0·1°; [I] 5·3 *mole l.*$^{-1}$.

Time (hrs.) ...	0·5	1·0	1·5	2·0	3·0	4·0	5·0	6·0	16·0	40·0
$E^{1\%}_{1\,\text{cm.}\,3265}$ ...	162·7	296·0	420·8	526·7	700·4	831·2	951·7	1018	1194	1197
Mole % of (II)	12·4	22·5	32·0	40·0	53·2	63·1	72·3	77·3	90·7	90·9

(iv) *At* 200° ± 1°; [I] 5·2 *mole l.*$^{-1}$.

Time (hrs.) ...	0·25	0·50	0·75	1·05	1·5	2·0	3·0	6·0	48·0 *
$E^{1\%}_{1\,\text{cm.}\,3265}$ ...	302·8	546·8	702·8	887·0	1012	1088	1158	1156	1147
Mole % of (II)	23·0	41·5	53·4	67·4	76·8	82·6	87·9	87·8	87·1

(II; R = *Allyl*):	(v) *At* 160° ± 0·5°.		(vi) *At* 180° ± 0·5°	
Time (hrs.) ...	96	144	20	40
$E^{1\%}_{1\,\text{cm.}\,3265}$ ...	1220	1224	1199	1193
Mole % of (II)	92·6	92·9	91·1	90·6

* Considerable darkening of product, suggestive of minor side reaction which may explain low result.

TABLE 13. *Reversible isomerisation of* (I; R = trans-*but-2-enyl*) *at* 200° ± 1°.

Time (hrs.)	5·0	20·0	48·0	96·0
$E^{1\%}_{1\,\text{cm.}\,2815}$	497·7	375·2	239·8	193·8
$E^{1\%}_{1\,\text{cm.}\,3265}$	236·8	524·2	830·7	923·0
Mole % of (III)	~0	2·0	3·7	—
Mole % of (I)	80·0	55·2	28·0	—
Mole % of (II)	19·4	41·5	65·3	—

isomerisations obeying equation (i) a linear plot of $\log_{10}\,[E^{1\%}_{1\,\text{cm.}\,3265e} - E^{1\%}_{1\,\text{cm.}\,3265t}]$ against t, of slope $-\,0{\cdot}4343(k_1 + k_2)$, should be obtained.

Reaction of cyclo*Hexyl Bromide with* (I; R = Me).—The sulphide (4·53 g., 0·025 mole) and the bromide (4·89 g., 0·03 mole) were heated at 200° ± 1° for 7·0 hours in an oxygen-free atmosphere in an apparatus sealed by mercury traps and connected to a liquid-air trap. A gaseous product, probably methyl bromide, was evolved throughout the reaction period. The main product, on alkali-extraction, gave (III) (0·893 g., 0·21 mol.), m. p. 177·5—178·5°, mixed m. p. 178—179°. Removal of the solvent and unchanged bromide and trituration of the product (3·9 g.) with concentrated hydrochloric acid gave: (i) a mixture (1·7 g.) of (I; R = Me) (~55%) and (I; R = *cyclo*hexyl) (~45%) (Found: C, 58·3; H, 5·15; N, 7·0; S, 29·5. Calc. for above mixture: C, 58·3; H, 5·05; N, 6·55; S, 30·1%); and (ii) a mixture (1·45 g.) of (II; R = Me) (~70%) and (II; R = *cyclo*hexyl) (~30%) [Found: C, 55·55; H, 4·55; N, 7·0; S, 32·25. Calc. for above mixture: C, 55·9; H, 4·5; N, 7·1; S, 32·5%).

Reaction of Di(*benzothiazol*-2-*yl*) *Disulphide with Dibenzyl.*—A mixture of the disulphide and dibenzyl was heated *in vacuo* at 200° ± 0·5° or 230° ± 1° for the appropriate times. The (III) formed was isolated and estimated by alkali-extraction (Part I). *trans*-Stilbene was estimated by ultra-violet spectrometry of the residue, after removal of (III), the absorption intensity being determined at 2950 Å where *trans*-stilbene has a maximum [$E^{1\%}_{1\,\text{cm.}\,2950}$, 1654], and the residue being assumed to consist of *trans*-stilbene and dibenzyl ($E^{1\%}_{1\,\text{cm.}\,2950}$, 6·0). The estimates of *trans*-stilbene so obtained are maximum values since enhanced absorption at 2815 and 3265 Å indicates the presence of other constituents which absorb at 2950 Å.

The disulphide (13·28 g., 0·04 mole) and dibenzyl (7·28 g., 0·04 mole), heated at 200° ± 0·5° for 48·0 hours, gave (III) (11·53 g., 0·069 mole) and a residue (8·69 g.) containing $\leqslant$40% of *trans*-stilbene [Found: C, 85·85; H, 6·0; N, 1·60; S, 6·55%; *M* (ebullioscopic, in benzene), 225, 241]. Light absorption: max., 2950 Å; $E^{1\%}_{1\,\mathrm{cm.}\,2950}$, 667·2, $E^{1\%}_{1\,\mathrm{cm.}\,2815}$, 572·0, $E^{1\%}_{1\,\mathrm{cm.}\,3265}$, 283·2. A portion (7·27 g.) of the residue on distillation gave: (i) b. p. 80—110°/0·005 mm. (2·50 g.), containing $\leqslant$25·5% of *trans*-stilbene [Found: C, 90·5, 90·4; H, 7·1, 7·25; N, 0·45; S, 1·1%; *M* (ebullioscopic, in benzene), 161, 182, 183; Light absorption: max., 2950 Å; $E^{1\%}_{1\,\mathrm{cm.}\,2950}$, 424·0, $E^{1\%}_{1\,\mathrm{cm.}\,2815}$, 351·2, $E^{1\%}_{1\,\mathrm{cm.}\,3265}$, 131·6]; (ii) b. p. 110—130°/0·005 mm. (1·52 g.), containing $\leqslant$86% of *trans*-stilbene [Found: C, 90·25; H, 6·6; N, 0·85; S, 2·1%; *M* (ebullioscopic, in benzene), 187, 188, 197; Light absorption: max., 2950 Å; $E^{1\%}_{1\,\mathrm{cm.}\,2950}$, 1424; $E^{1\%}_{1\,\mathrm{cm.}\,2815}$, 1166; $E^{1\%}_{1\,\mathrm{cm.}\,3265}$, 482·3]; and a residue (3·02 g.) containing a dehydropolymer of dibenzyl and 2-mercaptobenzothiazole derivatives [Found: C, 78·95, 78·8; H, 4·85, 4·8; N, 2·5; S, 12·35, 12·5%; *M* (ebullioscopic, in benzene), 314, 348. Light absorption: max., ~3100 Å].

The yields of (III) and the maximum yields of *trans*-stilbene obtained under other reaction conditions are given below.

Reaction of Di(benzothiazol-2-yl) Disulphide with Dibenzyl.

Temp.	Time (hrs.)	Disulphide (10^3 Mole.)	Dibenzyl (10^3 Mole.)	(III) (10^3 Mole.)	Residue (g.)	$E^{1\%}_{1\,\mathrm{cm.}\,2950}$	Max. % of *trans*-stilbene
200° ± 0·5°	24·0	5	5	8·4	—	—	—
230° ± 1°	8·0	5	20	8·8	3·63	241·0	14
,,	24·0	5	20	8·9	3·70	242·5	14
,,	24·0	5	5	9·4	—	—	—

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