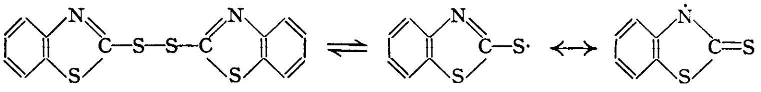
813. *2-Mercaptobenzothiazole Derivatives. Part I. The Reaction of Di(benzothiazol-2-yl) Disulphide with Olefins.*

By C. G. Moore.

The reaction of di(benzothiazol-2-yl) disulphide (I) with *cyclo*hexene at 139° yields 2-mercaptobenzothiazole (II), 2-(*cyclo*hex-2-enylthio)benzothiazole (III), and 3-(*cyclo*hex-2-enyl)-2-thiobenzothiazoline (IV). A brief kinetic study of the reaction supports a free-radical chain mechanism. The influence of olefin structure and concentration on the extent and course of the reaction is discussed and, in particular, the reaction of (I) with rubber is considered.

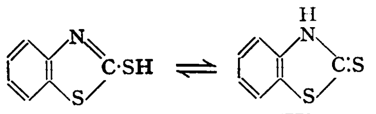
It has been frequently suggested that organic disulphides such as diphenyl disulphide and di(benzothiazol-2-yl) disulphide (I), on being heated in inert solvents, undergo reversible homolysis of the disulphide bond to give RS• radicals, which in the latter case are the mesomeric thiobenzothiazolyl radicals (I*a* ⟷ *b*) :



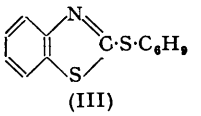
(I) (I*a*) (I*b*)

Evidence for this has been adduced from many experimental sources: *e.g.*, the fact that hot solutions of the disulphides are thermochromic and disobey Beer's law (Schönberg, Rupp, and Gumlich, *Ber.*, 1933, **66**, 1932; Schönberg and Rupp, *Naturwiss.*, 1933, **21**, 561; Koch, *J.*, 1949, **394**, 401), the behaviour on pyrolysis, and the dehydrogenation of benzyl alcohol to benzaldehyde by diphenyl disulphide with formation of thiophenol (Schönberg and Mustafa, *J.*, 1949, 889; *J. Amer. Chem. Soc.*, 1951, **73**, 2401). Ritter and Sharpe's observation (*ibid.*, 1937, **59**, 2351) that disulphides act as effective high-temperature dehydrogenators of hydrocarbons is also best explained on the basis of RS• radical formation. More compelling physicochemical evidence for the coexistence, in equilibrium, of the disulphide (I) and its derived thiobenzothiazolyl radicals (I*a* $\longleftrightarrow$ *b*) is that hot solutions of (I) in toluene are paramagnetic (Cutforth and Selwood, *ibid.*, 1948, **70**, 278).

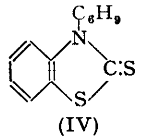
Little work has hitherto been reported on the thermal reaction of (I) and related disulphides with olefins. Farmer and Shipley (see Bloomfield, *J.*, 1947, 1547) showed that 2-mercaptobenzothiazole (II) was a major product of the reaction of (I) with *cyclo*hexene at 140° but no detailed study of the reaction was attempted. Diphenyl disulphide, on the other hand, is entirely without action on this olefin at 180° (Bloomfield, *loc. cit.*). More recently, Barton (*Ind. Eng. Chem.*, 1950, **42**, 671) found 85% reaction of (I) with rubber at 110°, the disulphide appearing as (II). It is of importance that the reaction leading to (II) did not result in cross-linking (vulcanisation) of the rubber.



(II*a*) (II*b*)



(III)

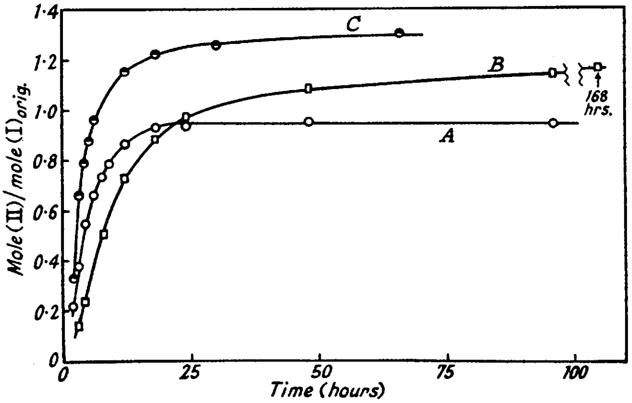


(IV)

It has now been found that the reaction of (I) with *cyclo*hexene in the molar ratio of 1 : 10 at 139° gives (II), 2-(*cyclo*hex-2-enylthio)benzothiazole (III), and 3-(*cyclo*hex-2-enyl)-2-thiobenzothiazoline (IV). The physical properties and ultra-violet and infra-red spectra

TABLE 1. *Yields of products from the reaction of* (I) (0·01 *mole*) *with* cyclo*hexene* (0·10 *mole*) *at* 139·0° ± 1·0°.

Time (hours)	48·0	96·0
Products (*mole*)	—	—
2-Mercaptobenzothiazole (II)	0·00956	0·00968
2-(*cyclo*Hex-2-enylthio)benzothiazole (III)	0·0052	0·0052
3-(*cyclo*Hex-2-enyl)-2-thiobenzothiazoline (IV)	0·0038	0·0037

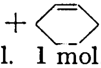


A, (I), 1 *mole*; cyclo*hexene*, 10 *moles*; [I], 0·735 *mole l.*$^{-1}$.

B, (I), 1 *mole*; cyclo*hexene*, 2 *moles in benzene*; [I], 0·737 *mole l.*$^{-1}$.

C, (I), 1 *mole*; 1-*methyl*cyclo*hexene*, 10 *moles*; [I], 0·637 *mole l.*$^{-1}$.

of (III) and (IV) thus isolated were very similar to those of synthetic samples. The yields of (II), (III), and (IV) (Table 1; Figure) indicate that under the reaction conditions used the stoicheiometry of the reaction closely follows equation (1);

(I) +  = (II) + [(III) + (IV)] . . . . . . (1)
1 mol. 1 mol. 1 mol. 1 mol.

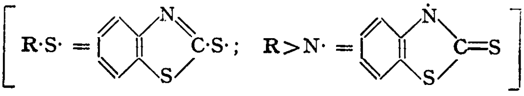
Mechanism of Reaction.—A brief study of the kinetics of the reaction has been made by estimating the yield of (II) as a function of time. The results support the following free-radical chain mechanism :

$$\mathrm{R{\cdot}S{\cdot}S{\cdot}R} \xrightarrow{k_1} \mathrm{2R{\cdot}S{\cdot}} \longleftrightarrow \mathrm{2R{>}N{\cdot}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(i)}$$

$$\mathrm{R{\cdot}S{\cdot}} \longleftrightarrow \mathrm{R{>}N{\cdot}} + \mathrm{C_6H_{10}} \xrightarrow{k_1} \mathrm{R{\cdot}SH} \rightleftharpoons \mathrm{R{>}NH} + \mathrm{C_6H_9{\cdot}} \quad . \; . \; . \; . \quad \text{(ii)}$$

$$\mathrm{R{\cdot}S{\cdot}S{\cdot}R} + \mathrm{C_6H_9{\cdot}} \xrightarrow{k_3} \left[\begin{array}{l} \rightarrow \mathrm{R{\cdot}S{\cdot}C_6H_9}\ \text{(III)} \\ \rightarrow \mathrm{R{>}N{\cdot}C_6H_9}\ \text{(IV)} \end{array} \right. + \mathrm{R{\cdot}S{\cdot}} \longleftrightarrow \mathrm{R{>}N{\cdot}} \quad . \; . \; . \quad \text{(iii)}$$

$$\mathrm{2C_6H_9{\cdot}} \xrightarrow{k_4} \mathrm{C_6H_9{\cdot}C_6H_9} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(iv)}$$



Application of the stationary-state concept to (i)—(iv) gives :

$$-\mathrm{d}[\mathrm{I}]/\mathrm{d}t = k_1[\mathrm{I}] + k_3\sqrt{2k_1/k_4} \, . \, [\mathrm{I}]^{3/2} \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

For *long chains* the first term in (2) becomes negligible and thus :

$$-\mathrm{d}[\mathrm{I}]/\mathrm{d}t = k_3\sqrt{2k_1/k_4} \, . \, [\mathrm{I}]^{3/2} \quad . \; . \; . \; . \; . \; . \quad (3)$$

which on integration gives :

$$\{[\mathrm{I}]_t^{-\frac{1}{2}} - [\mathrm{I}]_0^{-\frac{1}{2}}\} = 0{\cdot}5k_3t\sqrt{2k_1/\mathrm{k}_4} \quad . \; . \; . \; . \; . \; . \quad (4)$$

For equation (4) to be applicable the following relation must be closely satisfied :

$$[\mathrm{II}]_t = [\mathrm{I}]_0 - [\mathrm{I}]_t \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

In the reaction of (I) with *cyclo*hexene the final estimated yield of (II) [0·96—0·97 mole per mole of (I) decomposed] is in agreement with equation (5) and $[\mathrm{I}]_t$ can therefore be estimated from it by determining $[\mathrm{II}]_t$. When allowance was made for an initial induction period of *ca.* 1 hour a linear plot of $[\mathrm{I}]^{-\frac{1}{2}}$ so derived against *t* was obtained, indicating that the kinetic law (3) holds over an extensive range (*ca.* 20—80%) of the reaction. The composite rate constant, $k_3\sqrt{2k_1/k_4}$, has a value of $9{\cdot}5_5 \times 10^{-5}$ mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-1}$ at 139·0° ± 1·0°.

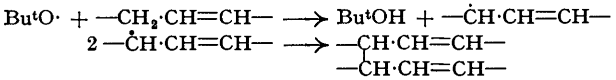
The fact that (III) and (IV) readily undergo mutual thermal isomerisation at 139°, leading to an equilibrium mixture of the two isomers (see Part II), prevents a decision as to the detailed mechanism of reaction (iii). Two radical substitution reactions are possible : (*a*) an $S_\mathrm{R}2$ mechanism, analogous to the ionic $S_\mathrm{N}2$ substitution, leading to (III) ; and (*b*) an $S_\mathrm{R}2'$ mechanism, analogous to the abnormal $S_\mathrm{N}2'$ substitution (Young, Webb, and Goering, *J. Amer. Chem. Soc.*, 1951, **73**, 1076, and references therein), leading to the isomeric compound (IV).

Influence of Reaction Conditions and Olefin Structure on $[\mathrm{II}]_{\mathrm{max.}}$.—Inspection of the data in the Figure indicates that the final yield of 2-mercaptobenzothiazole, $[\mathrm{II}]_{\mathrm{max.}}$, is dependent on both the reaction conditions and the structure of the olefin. Thus, reaction of (I) (1 mol.) with *cyclo*hexene (2 mols.) in benzene under disulphide concentration conditions equivalent to the non-diluted mixture raised the value of $[\mathrm{II}]_{\mathrm{max.}}$ to *ca.* 1·18 mole per mole of (I) decomposed. Whether this increase in $[\mathrm{II}]_{\mathrm{max.}}$ is due to the decreased olefin concentration or is the result of the intervention of benzene in the reaction cannot be decided on the available evidence. On replacement of *cyclo*hexene by 1-methyl*cyclo*hexene the change in the stoicheiometry of the reaction is even greater, a value of $[\mathrm{II}]_{\mathrm{max.}} =$ *ca.* 1·3 mole per mole of (I) decomposed being attained. These findings reveal that the rate equation (3) is no longer applicable in these cases. However, they are not necessarily inconsistent with the mechanism (i)—(iv) but may reflect an increase in the importance of the termination step (iv) compared with the second propagation step (iii), leading to a propagation sequence of short chain-length and the necessity to retain the first term in (2). No final statement as to the applicability or otherwise of the mechanism (i)—(iv) or the importance of the termination step (iv) can be made on the basis of the present data.

Barton's observation (*loc. cit.*) that the reaction of (I) with rubber does not lead to appreciable cross-linking (vulcanisation) suggests that the reported high value of $[\mathrm{II}]_{\mathrm{max.}}$ [1·7 mole per mole of (I) decomposed] is not the result of the increased importance of alkenyl-radical dimerisation (iv), a reaction tantamount to cross-linking of the rubber. Barton interprets the reaction as a dehydrogenation of the polyisoprene by (I) according to (6):

$$R'\dot{H}_x + R{\cdot}S{\cdot}S{\cdot}R = R'H_{(x-2)} + 2R{\cdot}SH \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It is reasonable to argue that polyisoprenyl radicals will be formed as the result of a reaction similar to (i) but not that these radicals will lead to a dehydrogenated rubber directly. This follows from the recent observation by Farmer and Moore (*J.*, 1951, 131, 142) that polyisoprenyl and related alkenyl radicals derived from the parent olefins by the action of *tert.*-butoxy-radicals at 100—140° participate almost entirely in coupling reactions, *e.g.*:



$$\mathrm{Bu^tO\cdot} + \mathrm{{-}CH_2{\cdot}CH{=}CH{-}} \longrightarrow \mathrm{Bu^tOH} + \mathrm{{-}\dot{C}H{\cdot}CH{=}CH{-}}$$

$$2\,\mathrm{{-}\dot{C}H{\cdot}CH{=}CH{-}} \longrightarrow \begin{array}{l}\mathrm{{-}CH{\cdot}CH{=}CH{-}}\\ \mathrm{{-}CH{\cdot}CH{=}CH{-}}\end{array}$$

The close similarity in conditions of radical production in these and in Barton's experiments makes it most improbable that there would be a major change in radical reactivity in the two systems.

The apparent inconsistencies can be reconciled if it is assumed (*a*) that the chain-mechanism (i)—(iv) is applicable in the case of rubber, (*b*) that the chain-length is long, leading to a minimum of cross-linking according to (iv), and (*c*) that the yield of (II) in considerable excess of 1 mole per mole of (I) decomposed is the result of a secondary thermal decomposition of the primarily formed polyisoprenyl analogues of (III) and (IV) leading to (II) and the dehydrogenated rubbber. The last assumption is consistent with the known ability of (III) and (IV) and related compounds to undergo thermal decomposition, leading to (II), as an alternative reaction to their mutual thermal isomerisation (Part II). The relative importance of the thermal decomposition reaction evidently depends on both the reaction temperature and the nature of the alkenyl substituent and it may well be that in the case of the polyisoprenyl analogues of (III) and (IV) the configurational conditions favour predominance of the decomposition.

EXPERIMENTAL

Materials.—*cyclo*Hexene, freshly distilled from sodium before use, had b. p. 82·5—82·7°/758—762 mm., n_D^{20} 1·4470 (Found: C, 87·8; H, 12·1; O, 0·12. Calc. for C_6H_{10}: C, 87·7; H, 12·3%); Infra-red analysis showed the absence of carbonyl and hydroxyl groups. 1-Methyl*cyclo*hexene had b. p. 109·2°/764 mm., n_D^{20} 1·4509 (Found: C, 87·2; H, 12·5; O, <0·1. Calc. for C_7H_{12}: C, 87·4; H, 12·6%). A commercial sample of di(benzothiazol-2-yl) disulphide (I), crystallised from benzene, had m. p. 178·5—179°. A sample of (I) prepared from pure (II) by iodine oxidation crystallised from benzene in colourless plates, m. p. 180—181° (Found: C, 50·8; H, 2·55; N, 8·4; S, 38·45. Calc. for $C_{14}H_8N_2S_4$: C, 50·6; H, 2·4; N, 8·4; S, 38·6%). Ultra-violet analysis showed that both samples contained <1% of (II).

Reaction of Di(benzothiazol-2-yl) Disulphide (I) *with* cyclo*Hexene.*—(*a*) The olefin (41·0 g., 0·5 mole) and the disulphide (16·60 g., 0·05 mole) were heated at $<10^{-3}$ mm. in a Carius tube at 139·0° ± 0·5° for 24·0 hours. After removal of unchanged olefin the product (19·55 g.) was dissolved in chloroform (200 ml.) and extracted with 10% aqueous sodium hydroxide (3 × 100 ml.). The first 200 ml. of alkaline extract on acidification (concentrated hydrochloric acid, 60 ml.) gave (II) (7·44 g., 0·0445 mole), which after crystallisation from water or ethanol had m. p. and mixed m. p. with an authentic sample, 179—180° (Found: C, 50·3; H, 3·1; N, 8·5; S, 38·7%; equiv., 168·0, 169·0. Calc. for $C_7H_5NS_2$: C, 50·3; H, 3·0; N, 8·4; S, 38·35%; equiv., 167·2). Acidification of the final 100 ml. of extract gave no further (II) showing that complete extraction of the thiol had been effected. The chloroform solution, after being washed with water, dried ($CaCl_2$), and freed from solvent, gave an orange viscous liquid (12·07 g.) which was rapidly distilled at as low a temperature as possible, giving as main fraction a light yellow oil, b. p. 140—170° (mainly 162—170°)/0·005 mm. (6·9 g.), which partly crystallised on storage. Separation of the mixture gave a filtrate (i) (4·7 g.), n_D^{20} 1·668, and a residue (ii) (2·2 g.).

The filtrate (i) consisted mainly of 2-(cyclo*hex-2-enylthio*)*benzothiazole* (III) together with *ca.* 4% of (II) and *ca.* 6% of 3-(cyclo*hex-2-enyl*)-2-*thiobenzothiazoline* (IV) (Found: C, 62·4;

H, 5·3; N, 5·8, 5·9; S, 26·25. $C_{13}H_{13}NS_2$ requires C, 63·1; H, 5·3; N, 5·7; S, 25·9%). Extraction of a portion (2·37 g.) of (i) in chloroform (50 ml.) with 10% aqueous sodium hydroxide (25 ml.) gave (II) (0·047 g., *i.e.*, 2%), m. p. 177—178°, mixed m. p. 177—178·5°. The alkali-insoluble portion, on removal of the solvent, gave almost pure (III) (2·21 g.), n_D^{20} 1·665 (Found: C, 62·8; H, 5·35; N, 6·2; S, 26·15%). The ultra-violet and infra-red spectra of this sample were identical with those of a synthetic sample of (III); a shoulder at ~3290 Å may be due to *ca.* 6% of (IV).

The residue (ii) was triturated with concentrated hydrochloric acid to remove traces of (III), and the resultant crystalline solid (2·1 g.) on alkali-extraction gave (II) (0·274 g.), m. p. and mixed m. p. 177—178°. The alkali-insoluble product (1·76 g.) was 3-(*cyclo*hex-2-enyl)-2-thiobenzothiazoline (IV) which crystallised from ethanol in light yellow prisms, m. p. and mixed m. p. with synthetic sample, 148·0° (Found: C, 63·15; H, 5·3; N, 5·9; S, 25·6%). The ultra-violet and infra-red spectra were identical with those of the synthetic sample.

The residue (5·02 g.) from the original distillation was shown by alkali-extraction to contain (II) (0·41 g.). The resultant alkali-insoluble product (4·55 g.) was a deep orange-brown oil which was not further examined.

(*b*) The olefin (8·21 g., 0·10 mole) and the disulphide (3·32 g., 0·01 mole) were heated at 139·0° ± 0·5° for (i) 48·0 and (ii) 96·0 hours. After removal of the unchanged olefin, (II) was quantitatively extracted with aqueous sodium hydroxide by the method described below. The alkali-insoluble product, after removal of the chloroform, was weighed, made up to a standard solution in ethanol, and analysed for (III) and (IV) by the ultra-violet spectrometric method described in Part II. The yields of the various products are given in Table 1.

Synthesis of 2-(cyclo*Hex-2-enylthio)benzothiazole* (III) *and* 3-(cyclo*Hex-2-enyl)-2-thiobenzothiazoline* (IV).—(*a*) A methanolic solution of 2-sodiothiobenzothiazole was made from anhydrous sodium methoxide (28·7 g., 0·53 mole) and (II) (88·9 g., 0·53 mole) under nitrogen. The methanol was replaced by pure toluene and to the resultant suspension, held at 80—90°, was added 3-bromo*cyclo*hexene (100·0 g., 0·62 mole; b. p. 57—58°/12 mm., n_D^{20} 1·5271) during 0·5 hour. After reaction for a further 6 hours at 80—90° the mixture was poured into water, and the toluene layer separated, extracted with 10% aqueous sodium hydroxide, washed with water, and finally dried ($CaCl_2$). Removal of the solvent and distillation of the product gave a mixture of (III) and (IV) (77·0 g., 59%), b. p. 157—159°/0·1 mm., as a light-yellow oil, which partly crystallised during one week under nitrogen. The solid was filtered off, washed with concentrated hydrochloric acid and then water, and extracted with alkali to remove (II) formed in the distillation. Crystallisation of the resultant solid from ethanol gave pure (IV) (27·6 g.) as light-yellow prisms, m. p. 148·0° (Found: C, 63·05; H, 5·35; N, 5·5; S, 25·75%). The filtrate, after similar extraction with alkali, gave (III) (30·1 g.; n_D^{20} 1·6666) containing 4·8% of (IV) [Found: C, 63·0; H, 5·25; N, 5·75; S, 25·75%; Light absorption (in ethanol): max. 2820, 2910, 3010 Å; ε, 13,120, 12,540, 11,000 respectively; $E^{1\%}_{1\,\text{cm.}\,2815}$, 527·5; $E^{1\%}_{1\,\text{cm.}\,3265}$, 52·8]. On the basis of these values $E^{1\%}_{1\,\text{cm.}\,2815} = 550·0$ for pure (III).

(*b*) The same compounds were obtained by treating 2-sodiothiobenzothiazole [from (II), 75·2 g., 0·45 mole; sodium methoxide, 24·3 g., 0·45 mole] in ethanol (100 ml.) with the bromide (75·8 g., 0·47 mole) at 85° for 2·0 hours under nitrogen. The concentrations of the reactants (sodio-salt ~2·3M; bromide ~2·4M) were those conducive to an S_N2 reaction. The product, worked up as described above, gave (III) (26·2 g., 24%), n_D^{20} 1·6659 [Found: C, 63·1, 63·05; H, 5·3, 5·35; N, 5·7; S, 25·75%; Light absorption (in ethanol): $E^{1\%}_{1\,\text{cm.}\,2815}$, 522·3; $E^{1\%}_{1\,\text{cm.}\,3265}$, 61·0], containing 5·6% of the isomer (IV). On the basis of this value the $\varepsilon_{\text{max.}}$ and $E^{1\%}_{1\,\text{cm.}}$ values for pure (III) are $\varepsilon_{2820} = 13{,}600$; $\varepsilon_{2910} = 12{,}940$; $\varepsilon_{3010} = 11{,}160$; $E^{1\%}_{1\,\text{cm.}\,2815} = 548·3$. The pure (IV) (14·4 g., 13%) had m. p. 147—148° [Found: C, 63·0; H, 5·45; N, 5·8; S, 25·7%; Light absorption (in ethanol): max. 2420, 3270 Å; $\varepsilon_{2420} = 12{,}640$; $\varepsilon_{3270} = 26{,}200$; $E^{1\%}_{1\,\text{cm.}\,2815}$, 88·8; $E^{1\%}_{1\,\text{cm.}\,3265}$, 1058].

Reaction Kinetics.—(a) *Estimation of 2-mercaptobenzothiazole* (II). The sample for analysis of (II) was dissolved in chloroform (100 ml.), cooled to 0°, and extracted, by vigorous shaking for 10 minutes, with 10% aqueous sodium hydroxide (25·0 ml.). The alkaline extract was separated, the separating funnel was washed with water (2 × 5 ml.) followed by concentrated hydrochloric acid (15 ml.), and both washings were added to the alkaline extract. Next morning the precipitated (II) was filtered off (Gooch), washed with water (3 × 5 ml.), and dried to constant weight at 100—120°. The representative results given in Tables 2 and 3 indicate the applicability of the above procedure for estimation of (II) in the range 0·4—2·3 g. in admixture with (I), (III), and (IV).

(b) *Reaction of* (I) *with* cyclo*hexene.* The disulphide and the olefin were heated at

Table 2.

(II) (g.)	Recovery of (II) (%)	(II) (g.)	Recovery of (II) (%)	(II) (g.)	Recovery of (II) (%)	(II) (g.)	Recovery of (II) (%)
0·1006	93·9	0·6036	98·5	1·3002	99·2	1·9899	99·8
0·1882	96·7	0·8016	98·4	1·6212	99·2	2·2740	99·6
0·4018	98·2	1·0060	98·9	1·7162	99·2	—	—

Table 3.

(II) (g.)	(I) (g.)	(III) (g.)	(IV) (g.)	Recovery of (II) (%)
0·3890	1·5353	—	—	100·4
0·5875	1·0865	—	—	99·1
1·2274	0·5571	—	—	101·1
1·4244	0·3225	—	—	99·8
0·5003	2·3192	0·3704	0·3697	102·3
0·8300	1·6606	0·6196	0·6182	101·4
1·3396	0·6566	0·9912	0·9892	101·1
1·6710	—	1·2290	1·2308	99·6

Table 4. *Reaction of* (I) (3·32 *g.*, 0·01 *mole*) *with* cyclo*hexene* (8·21 *g.*, 0·10 *mole*) *at* 139·0° ± 1·0°. *Concn. of* (I), 0·735 *mole* $l.^{-1}$

Time (hours)	2·0	3·0	4·5	6·0	7·5	9·0	12·0	18·0	24·0	48·0	96·0
[II], mole $l.^{-1}$	0·160	0·279	0·402	0·486	0·539	0·578	0·637	0·686	0·690	0·705 *	0·703 †

* Mean of three determinations. † Mean of five determinations.

$<10^{-3}$ mm. and 139·0° ± 1·0° for the appropriate time. It was necessary to shake the reactants for the first hour to effect solution of the disulphide. The product, after removal of the unchanged olefin, was analysed for (II) by the procedure described above. The yields of (II) are given in Table 4 and the Figure.

The author thanks Drs. L. Bateman and G. Gee, F.R.S., for helpful advice and criticism, Dr. E. S. Waight and Miss J. M. Fabian for the spectroscopic data, and Mr. P. H. Tolcher for experimental assistance. Microanalyses were conducted under the supervision of Dr. W. T. Chambers.

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[*Received, April 25th,* 1952.]