The Reactions of Amines and Sulphur with Olefins. Part I. The Reaction of Diethylamine and Sulphur with cyclo*Hexene.*

By C. G. Moore and R. W. Saville.

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The reaction of diethylamine and sulphur with *cyclo*hexene at 140° yields di*cyclo*hexyl mono- and di-sulphides and saturated polymeric products, $C_6H_{11}\cdot S_x\cdot(C_6H_{10})\cdot S_x\cdot C_6H_{11}$, containing *cyclo*hexane units linked by sulphur, where x is 1 or 2. *N*-Ethylthioacetamide (IV) is formed as a major product, and minor products include *NN*-diethylthioacetamide (V) and diethylammonium hydrogen sulphide (VI); (IV)—(VI) are also formed by reaction of diethylamine with sulphur at 140°. The mechanisms of the olefin–sulphuration processes are discussed.

One of the main objectives of the work described in this group of papers is the utilisation of combinations of amine and sulphur to effect the sulphuration of mono- and $\Delta^{1:5}$-di-olefins. Examination of the rôle of the amine in determining the structural types of the sulphur linkages in the sulphurated product is of importance since upon such studies must be based a clearer understanding of the function of amines and derived basic compounds as accelerators of sulphur vulcanisation.

The formation of complexes between sulphur and secondary amines at room temperature was reported by Bedford (*India Rubber World*, 1921, **64**, 572; U.S.P. 1,719,920/1929) and by Levi (*Gazzetta*, 1930, **60**, 975; 1931, **61**, 286). It has now been found that treatment of such complexes with polar solvents, such as ethanol, *quantitatively* liberates the sulphur in an active form which converts sodium sulphite into thiosulphate at room temperature. Analogous behaviour is the action of piperidine at room temperature on variously constituted dialkyl tetrasulphides in removing a considerable proportion of the polysulphidic sulphur in the form of the complex, the tetrasulphide being largely converted into disulphide. Several workers (Kratz, Flower, and Coolidge, *Ind. Eng. Chem.*, 1920, **12**, 317; Bedford and Scott, *ibid.*, 1921, **13**, 126) have suggested that the accelerating effect of amines in rubber vulcanisation is due to the thermal liberation of active sulphur. However, attempts to sulphurise *cyclo*hexene at 60—80° with the complexes from sulphur and various secondary amines proved unsuccessful, and it thus seems unlikely that liberation of active sulphur under these conditions is occurring. Attention was therefore directed to the sulphuration capabilities of the amine–sulphur combination at 140°.

Reaction of *cyclo*hexene with diethylamine and sulphur at 140° gave a high yield of sulphurated products which consisted mainly of di*cyclo*hexyl monosulphide, together with a smaller amount of the disulphide; *cyclo*hexanethiol and di*cyclo*hexyl polysulphides having three or more sulphur atoms in the cross-link were formed in negligible amount. A mixture of saturated polymeric products containing three or more *cyclo*hexane units linked by mono- or di-sulphide bridges, *e.g.*, $C_6H_{11}\cdot S_{1-2}\cdot C_6H_{10}\cdot S\cdot C_6H_{11}$ (I), was also obtained, and identified by elementary and infra-red spectroscopic analysis, by molecular-weight determination, and by examination of the products resulting from its reduction with lithium aluminium hydride (Arnold, Lien, and Alm, *J. Amer. Chem. Soc.*, 1950, **72**, 731). This treatment gave *cyclo*hexanethiol, a thiol sulphide, $C_6H_{11}\cdot S\cdot C_6H_{10}\cdot SH$ (II), and an unreducible polymeric material containing monosulphide bridges, *viz.*, $C_6H_{11}\cdot S\cdot C_6H_{10}\cdot S\cdot C_6H_{11}$ (III). There was no evidence for the presence in the reduction product of *cyclo*hexanedithiol which would have resulted from a polymer of the type $C_6H_{11}\cdot S_2\cdot C_6H_{10}\cdot S_2\cdot C_6H_{11}$. It is noteworthy that a sulphurated polymer, obtained from unaccelerated sulphur–olefin interaction, was reported by Armstrong, Little, and Doak (*Ind. Eng. Chem.*, 1944, **36**, 628) but was not examined.

The fully saturated and predominantly mono- and di-sulphidic nature of the present products contrasts markedly with the apparent alkyl alkenyl nature of the polysulphide obtained by Farmer and Shipley (*J.*, 1947, 1519) from the reaction of sulphur with *cyclo*hexene at 140° (cf. Selker and Kemp, *Ind. Eng. Chem.*, 1947, **39**, 895). On the other hand, the present results recall the work of Naylor (*J.*, 1947, 1532) who found that polar addition of hydrogen sulphide to mono-olefins at 140° gave alkanethiols and alkyl mono- and disulphides, though in yields considerably inferior to those now obtained.

Sulphurated nitrogenous compounds, derived from the reaction of diethylamine and sulphur, were isolated and characterised as *N*-ethylthioacetamide (IV), *NN*-diethylthioacetamide (V), and diethylammonium hydrogen sulphide (VI), the last two compounds being isolated in minor amounts only. The possible formation of *NN'*-thiobisdiethylamine, $S(NEt_2)_2$ (VII), and of the corresponding polysulphides was ruled out since an authentic sample of (VII) readily formed a crystalline, water-soluble thionate with sulphurous acid (Lecher, Weigel, and Wittner, G.P. 517,995/1927), whereas this reagent failed to remove the nitrogenous component from the di*cyclo*hexyl sulphide fractions. Infra-red spectroscopic examination also failed to reveal the presence of any *NN'*-thioamines $(Et_2N)_2S_x$. The existence of both thione and thiol forms of (IV), $CH_3\cdot CS\cdot NHEt$ and $CH_3\cdot C(\cdot SH){:}NEt$, suggested the possible formation of the *cyclo*hexylthio-derivative, $CH_3\cdot C({:}NEt)\cdot S\cdot C_6H_{11}$, by reaction of (IV) with *cyclo*hexene, but no evidence of such addition was found. Similarly, diethyl*cyclo*hexylamine was not formed when diethylamine was heated with *cyclo*hexene at 140°, in contrast to the known addition of amines to activated double bonds (Bieber, *Compt. rend.*, 1950, **231**, 291).

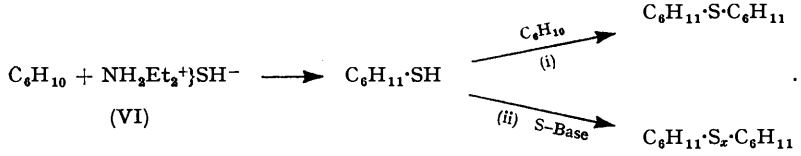
Independent investigation of the reaction of diethylamine and sulphur at 140° revealed that both (IV) and (VI) were major products, formed by replacement of the α-methylenic hydrogen atoms of the amine by sulphur, as represented formally by (1) :

$$CH_3\cdot CH_2\cdot NHEt + 2S \longrightarrow H_2S + CH_3\cdot CS\cdot NHEt \quad \text{(IV)} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

A minor product of this reaction was (V), whose formation is attributed to the alkylation process (2). This compound also resulted from the reaction between sulphur and triethylamine at 140° (cf. Levesque, U.S.P. 2,560,296/1951).

$$NHEt_2 + CH_3\cdot CS\cdot NHEt \longrightarrow NH_2Et + CH_3\cdot CS\cdot NEt_2 \quad \text{(V)} \quad . \quad . \quad . \quad . \quad (2)$$

Mechanism of the cyclo*Hexene Sulphuration Reaction.*—It is considered that a major sulphurating agent in the reaction at 140° of diethylamine and sulphur with *cyclo*hexene is diethylammonium hydrogen sulphide (VI). Polar addition of (VI) to the olefin gives *cyclo*hexanethiol, which then undergoes : (i) further polar addition to give di*cyclo*hexyl monosulphide, and (ii) base-catalysed oxidation by sulphur to give di*cyclo*hexyl di- and poly-sulphides and more hydrogen sulphide, a reaction known to be rapid even at room temperature (Bloomfield, *J. Soc. Chem. Ind.*, 1948, **67**, 14; McMillan and King, *J. Amer. Chem. Soc.*, 1948, **70**, 4143) :



$$C_6H_{10} + \underset{\text{(VI)}}{NH_2Et_2^+\}SH^-} \longrightarrow C_6H_{11}\cdot SH \begin{cases} \xrightarrow[\text{(i)}]{C_6H_{10}} C_6H_{11}\cdot S\cdot C_6H_{11} \\ \xrightarrow[\text{(ii) S-Base}]{} C_6H_{11}\cdot S_x\cdot C_6H_{11} \end{cases} \quad . \quad . \quad (3)$$

Compelling evidence for the ionic course of these reactions is presented in Part II (following paper), where it is shown that the thiols and sulphides obtained from the comparable sulphuration of trialkylethylenes invariably have a *tert.*-alkyl configuration.

The absence of *cyclo*hexanethiol, in contrast to the results of Naylor (*loc. cit.*), and the isolation of a considerable proportion of the monosulphide indicate the ease with which path (i) is followed. This was initially considered to be due to base catalysis of addition of hydrogen sulphide and thiol to the olefin, especially since such catalysis has already been observed (Foldi and Kollonitsch, *J.*, 1948, 1683; Dahlbom, *Acta Chem. Scand.*, 1951, **5**, 690). However, this explanation is inadequate since reaction of (VI) with *cyclo*hexene at 140° in the presence of a small amount of sulphur gives poor yields of the thiol and monosulphide, with high recovery of hydrogen sulphide.

The predominantly disulphidic nature of the di*cyclo*hexyl polysulphide fraction is probably due to two factors : first, the insufficiency of sulphur, through its prior reaction with the amine (higher polysulphides are formed only when high proportions of sulphur are available in the base-catalysed thiol oxidation); and secondly, the removal of the central sulphur atoms in the polysulphide by the amine as referred to above (p. 2082). The sulphur so removed becomes available for reaction with the amine according to (1) and for subsequent olefin sulphuration processes. The absence of any reaction between dialkyl disulphides and secondary amines at 140°, however, precludes the possibility of any di*cyclo*hexyl monosulphide being formed by a sulphur-stripping process of the above type.

Undoubtedly olefin–sulphur interaction leading to alkyl alkenyl polysulphides (Farmer and Shipley, *loc. cit.*) competes initially with the amine–sulphur and ensuing addition reactions depicted above, and such competition may well be facilitated by amine catalysis since it is known that amines increase the rate of sulphur–rubber combination (*e.g.*, Williams, *Ind. Eng. Chem.*, 1947, **39**, 901). However, the exclusively saturated nature of the products indicates that the *cyclo*hexenyl *cyclo*hexyl polysulphide initially formed must undergo further additive sulphuration by means of (VI) and *cyclo*hexanethiol, and thus acts as the precursor of the observed saturated polymeric sulphides (4). The mono- and di-sulphidic nature of the sulphur linkages in the polymer is again due to the incursion of the amine–polysulphide desulphuration process described above :

$$\begin{tikzcd}
 & C_6H_{11}\cdot S_x\cdot C_6H_{10}\cdot SH \arrow[r, "\text{S–Base}"] \arrow[d, "C_6H_{10}"] & (C_6H_{11}\cdot S_x\cdot C_6H_{10}\cdot S\text{–})_2 \\
C_6H_{11}\cdot S_x\cdot C_6H_9 \arrow[ur, "(VI)"] \arrow[dr, "C_6H_{11}\cdot SH"'] & & \\
 & C_6H_{11}\cdot S_x\cdot C_6H_{10}\cdot S\cdot C_6H_{11} &
\end{tikzcd} \qquad . \quad . \quad (4)$$

It is believed that olefinic sulphuration processes of the above type would occur, with only minor modifications, were diethylamine to be substituted by most classes of aliphatic and aromatic amines since the latter readily liberate hydrogen sulphide on reaction with sulphur at elevated temperatures (Levesque, *loc. cit.*; Hodgson, *J.*, 1924, **125**, 1855; Johnson and Moore, *J. Amer. Chem. Soc.*, 1935, **57**, 1287; McMillan and King, *loc. cit.*; Brace, *ibid.*, 1953, **75**, 357). Only the combined absence of amino-hydrogen and methylene groups vicinal to the nitrogen atom prevents the formation of hydrogen sulphide (Johnson and Moore, *loc. cit.*). An example of this class of amine is dimethylaniline, and it is noteworthy that reaction of this amine with *cyclo*hexene and sulphur at 140° yielded alkyl alkenyl polysulphides comparable to those obtained from the *cyclo*hexene–sulphur reaction. This finding further supports the view that diethylamine–sulphur interaction according to (1) is an essential prior step to the subsequent additive sulphuration of the olefin by (VI) and *cyclo*hexanethiol.

Sulphuration of Olefins with NN′-*Thiobisamines*.—Bedford (*loc. cit.*) was the first to show that *NN*′-thiobisamines effectively vulcanise rubber, and this has since been confirmed by Blake (U.S.P. 2,325,735/1943), Hand (U.S.P. 2,490,518/1949), and Beaver and Throdahl (*Rubber Chem. Tech.*, 1944, **17**, 896; 1945, **18**, 110). More recently these compounds, particularly *NN*′-dithiobismorpholine, have come into prominence as vulcanising agents which impart reduced scorching and superior ageing characteristics to furnace-black stocks (Sibley, *ibid.*, 1951, **24**, 211; Throdahl and Harman, *Ind. Eng. Chem.*, 1951, **43**, 421). It is thus of importance to study the function of such compounds as olefinic sulphurating agents and the results of a preliminary study with *NN*′-thiobisdiethylamine (VII) are now described. Reaction of (VII) with *cyclo*hexene at 140° yielded di*cyclo*hexyl mono- and di-sulphides, diethylamine, and (IV), together with much unidentified material of high molecular weight. The reaction characteristics in this case thus closely resemble those of the diethylamine–sulphur–*cyclo*hexene system and it would seem that similar sulphurating mechanisms are operative. This conclusion is strengthened by the behaviour of (VII) on thermal decomposition at 140°, for diethylamine, (IV), (V), and (VI) were formed, the infra-red spectra of the reaction products being very similar to those from the diethylamine–sulphur reaction at 140°. Investigations are continuing of the olefinic-sulphuration capabilities and thermal decomposition characteristics of (VII) and related compounds.

EXPERIMENTAL

Infra-red spectra were recorded on a Grubb–Parsons single-beam spectrometer. Micro-analyses were conducted under the supervision of Dr. W. T. Chambers.

Materials.—*cyclo*Hexene, freed from peroxide and distilled from sodium under nitrogen, had b. p. 82·5—82·6°/755 mm., $n_{\rm D}^{20}$ 1·4472 (Found: C, 87·8; H, 12·25. Calc. for C_6H_{10}: C, 87·7; H, 12·3%). Infra-red analysis showed the absence of carbonyl and hydroxyl groups. Sulphur was purified by Bacon and Fanelli's method (*Ind. Eng. Chem.*, 1942, **34**, 1043). Diethylamine, dried (KOH) and fractionated, had b. p. 55·0°/765 mm., $n_{\rm D}^{20}$ 1·3855. Infra-red analysis confirmed the absence of triethylamine.

Action of Piperidine on Sulphur and Alkyl Tetrasulphides at Room Temperature. (With Drs. G. H. THOMAS and R. F. NAYLOR.)—A mixture of piperidine (10·0 g.) and sulphur (3·0 g.) in benzene (10 ml.) readily precipitated a dark orange complex on storage under nitrogen. Removal of the solvent and excess of piperidine by evaporative distillation *in vacuo* at room temperature yielded the *complex* as a dark orange, viscous oil (Found: C, 45·85; H, 7·5; N, 8·15. $C_{10}H_{22}N_2S_4,\frac{1}{2}C_6H_6$ requires C, 46·3; H, 7·4; N, 8·3%). Dilution of the complex, similarly derived from sulphur (3·2 g.) and piperidine (8·6 g.), with ethanol precipitated sulphur (3·1 g.), which on treatment with aqueous sodium sulphite rapidly dissolved to give sodium thiosulphate. Acidification of the ethanolic filtrate with ethanolic hydrogen chloride (15 g.; 40% solution) and evaporation *in vacuo* gave piperidine hydrochloride (9·7 g.), and extraction of the filtrate with water gave further sulphur (0·07 g.; total recovery 99%).

Di*iso*propyl tetrasulphide (6·4 g., 1 mol.), b. p. 67·5—70°/0·04 mm., $n_{\rm D}^{20}$ 1·5842 (Found: C, 33·55; H, 6·4; S, 60·15. Calc. for $C_6H_{14}S_4$: C, 33·6; H, 6·6; S, 59·8%), was mixed with piperidine (4 mol.) and kept at room temperature for 24 hr. under nitrogen. The dark brown product was taken up in ether and shaken successively with 40% aqueous sodium sulphite, water, 2N-hydrochloric acid, and aqueous sodium hydrogen carbonate. After drying ($MgSO_4$) and removal of the solvent, the product was distilled to give: (i) b. p. 56—59°/10 mm., $n_{\rm D}^{20}$ 1·4952 (1·52 g.) (Found: S, 43·65%), (ii) b. p. 60—65°/10 mm., $n_{\rm D}^{20}$ 1·5052 (1·29 g.) (Found: S, 46·5%), (iii) b. p. 45—60°/0·1 mm., $n_{\rm D}^{20}$ 1·5281 (1·47 g.) (Found: S, 51·35%), (iv) residue (0·19 g.) (Found: S, 51·9. Calc. for $C_6H_{14}S_2$: S, 42·7%. Calc. for $C_6H_{14}S_3$: S, 52·7%). Acidification of the sulphite extract gave sulphur (1·22 g.). The mild sulphite treatment used did not itself remove any of the combined sulphur of the tetrasulphide. Similar results were obtained with di-*n*-butyl, di-*tert.*-butyl, and dibenzyl tetrasulphides, the last giving ~70% of dibenzyl disulphide, m. p. 70—71° (Found: S, 26·0. Calc. for $C_{14}H_{14}S_2$: S, 26·0%). The ease of desulphuration of the tetrasulphides by piperidine followed the order: dibenzyl- > di-*n*-butyl- > di-*iso*propyl- > di-*tert.*-butyl-.

Attempted Low-temperature Sulphuration of cyclo*Hexene.*—A mixture of sulphur (5·0 g.), diethylamine (15 g.), and *cyclo*hexene (25 g.) was heated under nitrogen for 6 hr. at *ca.* 60°. Removal of excess of amine and olefin on the water-bath and addition of water to the residue gave unchanged sulphur (4·8 g.) and a liquid fraction which on distillation gave no sulphurated product. A similar reaction with piperidine at 55—60° for 4 hr. gave only a tar which slowly liberated sulphur with water. Use of di*cyclo*hexylamine at *ca.* 80° was likewise unsuccessful.

Reaction of Diethylamine and Sulphur at 140°.—A mixture of the amine (30 g.) and sulphur (10 g.) was heated at $<10^{-3}$ mm. in a Carius tube at 140° ± 1° with gentle shaking for 2½ hr. Diethylammonium hydrogen sulphide (9·3 g.) was filtered off under nitrogen from the liquid product, and after being washed with a little ice-cold ether and further purified by repeated vacuum-sublimation was identical with an authentic sample [m. p. and mixed m. p. (sealed-tube) 57—62°] (Achterhof, Conaway, and Boord, *J. Amer. Chem. Soc.*, 1931, **53**, 2682). No unreacted sulphur remained after the sublimation. The reddish-brown filtrate, after removal of unchanged amine, gave a product (15·4 g.), b. p. 62—68°/0·05 mm., shown by elementary and spectroscopic analysis to be mainly (IV) together with a little (V). When this material was heated with aqueous sodium hydroxide it gave ethylamine, and on refluxing for 1 hr. with 50% hydrochloric acid it gave hydrogen sulphide and acetic acid, the latter being identified by its *S*-benzylthiuronium salt, m. p. and mixed m. p. 136—137°. Raney nickel hydrogenolysis of the material gave diethylamine, identified as its toluene-*p*-sulphonyl derivative, m. p. and mixed m. p. 60°. Reaction with methyl iodide afforded a liquid methiodide which gave with alkali and subsequent fractionation N-*ethyl*-S-*methyl*iso*thioacetamide*, b. p. 44—48°/12 mm., $n_{\rm D}^{20}$ 1·4893 (Found: C, 51·55; H, 9·45; N, 11·9. $C_5H_{11}NS$ requires C, 51·3; H, 9·4; N, 11·9%). These reactions establish (IV) as a major component of the above material and this was confirmed by the close identity of its ultra-violet absorption spectrum with that of synthetic (IV).

A second experiment with the same quantities of amine and sulphur heated for 5 hr. at 140° ± 0·5° gave (VI), unreacted sulphur (6·6 g.), and the ligroin-insoluble material (5·1 g.) consisting of (IV) and (V), b. p. 66—67°/0·02 mm., n_D^{20} 1·5525 (Found: C, 49·5; H, 9·2; N, 12·4%).

Synthesis of N-*Ethylthioacetamide* (IV).—This compound, synthesised from ethylamine and either (*a*) thioacetamide or (*b*) *n*-propyl thionacetate, had b. p. 63—66°/0·02 mm., n_D^{20} 1·5590 (4·2 g.) (Found: C, 46·6; H, 8·9; N, 14·3. Calc. for C_4H_9NS: C, 46·6; H, 8·7; N, 13·6%). Light absorption: max., 2640, 3260 Å; ε, 1260, 5·4, respectively.

When (IV) was heated *in vacuo* at 140° ± 1° for 20 hr. it was recovered completely unchanged as revealed by elementary and infra-red analysis.

Reaction of Triethylamine and Sulphur at 140°.—Triethylamine (40 g.; b. p. 89·5°/759 mm.; n_D^{20} 1·4003) and sulphur (10 g.) were heated at $<10^{-3}$ mm. in a Carius tube at 140° ± 1° for 21 hr. After removal of carbonaceous matter (3·9 g.) in nitrogen, the filtrate was evaporated on the steam-bath under reduced pressure. Distillation of the residue gave (V), b. p. 68—70°/0·5 mm. (17·5 g.); redistillation gave a colourless liquid, b. p. 63—64°/0·1 mm., n_D^{20} 1·5445 (Found: C, 54·2; H, 9·7; N, 10·5; S, 25·3. Calc. for $C_6H_{13}NS$: C, 54·9; H, 9·9; N, 10·7; S, 24·4%).

Synthesis of NN-*Diethylthioacetamide* (V).—(1) *NN*-Diethylacetamide [5·75 g.; b. p. 70—72°/10 mm.; n_D^{20} 1·4390 (Found: C, 62·75; H, 11·55; N, 12·4. Calc. for $C_6H_{13}ON$: C, 62·6; H, 11·3; N, 12·2%)] was refluxed with phosphorus pentasulphide (2·3 g.) in benzene (20 ml.) for 10 min., to give (V), b. p. 55°/0·07 mm., n_D^{20} 1·5298 (4·5 g.) (Found: C, 54·3; H, 9·9; N, 11·1; S, 22·7. Calc. for $C_6H_{13}NS$: C, 54·9; H, 9·9; N, 10·7; S, 24·7%), containing a little of the unchanged amide. Comparison of the infra-red spectrum of this material with that of the sulphur–triethylamine product revealed practical identity: in particular, strong bands at 1282, 1242, 1031, 928, and 839 cm.$^{-1}$ were present in both spectra, but absent from the spectrum of (IV).

(2) On heating a mixture of (IV) (4·0 g.) and diethylamine (5·0 g.) *in vacuo* at 140° ± 1° for 20 hr. and fractionation of the product, there were obtained two fractions: (i) b. p. 53—66°/0·1 mm., n_D^{20} 1·5552 (2·1 g.) (Found: C, 47·3; H, 8·75; N, 13·7%), and (ii) b. p. 66—68°/0·1 mm., n_D^{20} 1·5595 (1·6 g.) (Found: C, 46·9; H, 8·8; N, 13·3%). The infra-red spectra of (i) and (ii) were practically identical and indicated that both were mainly unchanged (IV). However, five bands at 1282, 1242, 1031, 928, and 839 cm.$^{-1}$ (referred to above) indicated the presence of a minor amount of (V).

Reaction of Diethylamine and Sulphur with cyclo*Hexene at* 140°.—(1) The amine (30 g.), sulphur (10 g.), and the olefin (50 g.) were heated *in vacuo* ($<10^{-3}$ mm.) in a Carius tube at 140° ± 1° for 21 hr. with gentle rocking. The cooled product was filtered under nitrogen to remove (VI) (2·1 g.), and then freed from amine and olefin by evaporation under reduced pressure. Addition of excess of ligroin (b. p. 40—60°) precipitated an oil (i) (4·5 g.) and the main ligroin solution on extraction with 50% hydrochloric acid (3 × 25 ml.) gave an extract (ii). The ligroin solution was washed with aqueous sodium hydrogen carbonate, then water, and dried ($CaCl_2$). The absence of thiol in the solution was confirmed by a negative reaction with copper butyl phthalate. Removal of the solvent gave a main product (26·0 g.) which on fractionation in nitrogen gave fractions as shown in the Table. The final residue (ix) (2·20 g.) was dissolved in benzene and chromatographed on alumina. After elution with benzene, followed by ligroin containing 2% of ethanol, the solvent was removed from the eluate to give a clear, yellow glass which was dried at $<10^{-3}$ mm. [Found: C, 61·9; H, 8·35; N, 0·33; S, 30·4%; *M* (ebullioscopic in benzene), 520].

Fraction no.	B. p./mm.	Wt. (g.)	Found (%)				C : H	n_D^{20}	*M* (ebull. in C_6H_6)
			C	H	N	S			
(iii)	~60°/0·02 mm.	4·35	71·4	11·0	0·27	17·4	6 : 11	1·5181	190
(iv)	75—78°/0·05 mm.	5·41	71·55	11·05	0·32	17·4	6 : 11·1	1·5185	—
(v)	78—82°/0·05 mm.	3·30	69·85	10·75	0·44	18·85	6 : 11	1·5235	201
(vi)	Short-path distn. at 120—140°	2·0	64·2	9·4	0·40	26·45	6 : 10·5	1·5610	—
(vii)		4·6	64·05	9·3	0·38	26·3	6 : 10·4	1·5622	303
(viii)		2·3	63·5	9·2	0·37	27·2	6 : 10·4	1·5693	350
Calc. for $C_{12}H_{22}S$			72·7	11·1	0	16·2	6 : 11	—	198
Calc. for $C_{12}H_{22}S_2$			62·6	9·55	0	27·8	6 : 11	—	230

Examination of the Fractions.—Fraction (i) on distillation gave a main fraction, a colourless liquid (4·1 g.), b. p. 67—68°/0·05 mm., n_D^{20} 1·5485 (Found: C, 53·5; H, 9·35; N, 9·9; S, 26·6%), shown by infra-red analysis to be mainly *N*-ethylthioacetamide (IV), together with minor amounts of (V) and *cyclo*hexyl sulphides. The acidic extract (ii) was made just alkaline at

0°, and the resultant oil taken up in chloroform, dried (Na_2SO_4), and distilled, to give a main fraction, b. p. 58—60°/0·02 mm. (4·1 g.), n_{D}^{20} 1·5490 (Found: C, 52·0; H, 9·25; N, 12·1; S, 25·7%), shown by infra-red analysis to be (IV), with a minor amount of (V). The infra-red spectra, elementary analysis, and molecular weights of fractions (iii)—(ix) indicated that the earlier fractions (iii)—(v) were entirely di*cyclo*hexyl mono- and di-sulphides, and the later fractions (vi)—(ix) were saturated polymeric *sulphides* (I); the absence of unsaturation due to *cyclo*hexenyl groups was definitely established. The ultra-violet absorption of the recovered olefin indicated only *ca.* 1% of benzene and negligible *cyclo*hexa-1 : 3-diene.

Hydrogenolysis of the Sulphurated Polymer.—The sulphurated polymeric fractions, typified by (vi)—(ix) above, from various experiments were combined and chromatographed on alumina as described for (ix) [Found: C, 64·2; H, 9·2; S, 26·0%; *M* (ebullioscopic in benzene), 315. Calc. for $C_{18}H_{32}S_3$: C, 62·8; H, 9·3; S, 27·9%; *M*, 344. Calc. for $C_{18}H_{32}S_2$: C, 69·2; H, 10·25; S, 20·5%; *M*, 312]. The polymer (8·0 g.) was slowly added to a stirred suspension of lithium aluminium hydride (4·0 g.) in tetrahydrofuran (100 ml.) and then refluxed for 3 hr. On decomposition with ice and 2N-sulphuric acid no hydrogen sulphide was evolved, indicating the complete absence of polysulphide groups. Working up of the product in the usual way gave a material which on fractionation yielded: (i) *cyclo*hexanethiol, b. p. ~74°/42 mm. (1·75 g.), n_{D}^{20} 1·4830 (Found: C, 62·4; H, 10·4; S, 26·4%; C : H, 6 : 12. Calc. for $C_6H_{12}S$: C, 62·1; H, 10·3; S, 27·65%), containing a trace of tetrahydrofuran [infra-red analysis confirmed the presence of both these compounds, and treatment of (i) with hot aqueous mercuric cyanide yielded the mercuric salt, m. p. and mixed m. p. with an authentic sample, 71°]; (ii) b. p. 90°/0·05 mm. (2·30 g.), n_{D}^{20} 1·5502 [Found: C, 62·5; H, 9·35; S, 26·65; SH, 15·6%; *M* (ebullioscopic in benzene), 214. Calc. for $C_{12}H_{22}S_2$: C, 62·6; H, 9·55; S, 27·8; SH, 14·3%; *M*, 230]; and (iii) distilled in a short-path still at 120—135° (3·1 g.), n_{D}^{20} 1·5530 [Found: C, 67·8; H, 9·8; S, 21·75%; *M* (ebullioscopic in benzene), 293. Calc. for $C_{18}H_{32}S_2$: C, 69·2; H, 10·25; S, 20·5%; *M*, 312]. Infra-red analysis of (ii) showed the complete absence of unsaturated groups and the spectrum resembled that of the original sulphide in many respects, except that a strong thiol band was now present due to the *thiol sulphide* (II). Similar examination of (iii) indicated that this fraction contained little thiol, but was otherwise generally similar to (ii). The spectrum was almost identical with that of the original sulphurated polymer and the combined analytical and spectroscopic data indicate (iii) to be mainly the di*cyclo*hexylthio*cyclo*hexane (III). The thiol content of (ii) is slightly higher than is consistent with pure (II) and this must be attributed to the presence of *cyclo*hexanethiol or, possibly, to traces of *cyclo*hexanedithiol, but positive evidence was lacking for the latter.

(2) Repetition of the sulphuration process as described under (1) above, except for a reaction time of 5 hr., gave the ligroin-insoluble oil and (VI), together with a main sulphide product (20·4 g.). The latter was extracted with 15% sulphurous acid, washed with water, dried, and fractionated to give: (i) b. p. 60—65°/0·04 mm. (3·8 g.), n_{D}^{20} 1·5400 (Found: C, 57·05; H, 9·9; N, 8·5; S, 22·6%); (ii) b. p. 65—95°/0·04 mm. (3·55 g.), n_{D}^{20} 1·5360 (Found: C, 62·85; H, 10·15; N, 4·5; S, 21·85%); (iii) b. p. 95—105°/0·04 mm. (1·35 g.), n_{D}^{20} 1·5488 (Found: C, 62·15; H, 9·35; N, 0·82; S, 27·3%); (iv) "molecular" distillate (1·60 g.), n_{D}^{20} 1·5740 (Found: C, 60·2; H, 8·7; N, 1·0; S, 30·2%); (v) "molecular" distillate (1·61 g.), n_{D}^{20} 1·5772 (Found: C, 59·8; H, 8·7; N, 0·75; S, 30·85%); and a residue (vi) (5·30 g.), chromatographed in the usual manner [Found: N, 1·5; S, 33·05%; *M* (ebullioscopic in benzene), 458]. Prolonged extraction of (i) and (ii) with sulphurous acid failed to remove the nitrogenous material, and the acidic extract on evaporation was free from thionate. Infra-red analysis of (i)—(v) again confirmed *cyclo*hexyl sulphides to be major constituents, *cyclo*hexenyl groups definitely being absent. Comparison of the spectra with those of authentic *NN'*-thiobisamines $(Et_2N)_2S_x$ indicated the absence of the latter, the nitrogenous component being characterised as a mixture of the thioamides (IV) and (V).

Independent experiments showed (*a*) that treatment of *NN'*-monothiobisdiethylamine (VII) with 15% sulphurous acid readily gave the corresponding trithionate as white needles, m. p. 151°, from ethanol (cf. Lecher *et al.*, *loc. cit.*), and (*b*) that repeated extraction of an authentic mixture of (VII) and di*cyclo*hexyl monosulphide with 15% sulphurous acid effected complete separation of the two components, the former being obtained as the corresponding water-soluble trithionate in 90—95% yield.

Reaction of Diethylammonium Hydrogen Sulphide (VI) *with* cyclo*Hexene at* 140°.—Diethylamine (50 ml.), *cyclo*hexene (50 ml.), and sulphur (0·4 g.) were heated with hydrogen sulphide (~4·5 g.) in a nitrogen-filled Carius tube for 22 hr. at 140°. After removal of (VI) (4·2 g.) by filtration, fractionation gave (i) unchanged amine and olefin, b. p. 40—80°/760 mm., (ii) b. p.

60—80°/25 mm. (0·8 g.), n_D^{20} 1·4890 (Found : C, 67·15; H, 10·8; N, 0·43; S, 23·0%), (iii) b. p. 64—84°/0·1 mm. (2·2 g.), n_D^{20} 1·5272 (Found : C, 64·2; H, 10·45; N, 3·5; S, 20·9%). Infra-red analysis indicated that (ii) was mainly *cyclo*hexanethiol and (iii) a mixture of di*cyclo*hexyl sulphides and (V).

Reaction of Dimethylaniline and Sulphur at 140°.—When the amine (30 ml.) and sulphur (6·4 g.) were heated under reflux in nitrogen for 5 hr. at 140°, then cooled and filtered, the majority (5·8 g.) of the sulphur was recovered and the filtrate yielded only unchanged amine.

Reaction of Dimethylaniline and Sulphur with cyclo*Hexene*.—The amine (30 ml.), sulphur (5·0 g.), and olefin (25·0 g.) were heated in pure nitrogen for 5 hr. at 140°. Recovered sulphur (1·48 g.) was isolated on taking up the product in ice-cold ligroin. The filtrate was freed from solvent, and the residue fractionated to give : (i) recovered amine, b. p. 74—75°/11 mm. (35 g., 28·0 ml.), n_D^{20} 1·5587 (Found : C, 79·2; H, 9·05. Calc. for $C_8H_{11}N$: C, 79·3; H, 9·1%), and (ii) a dark viscous residue which was dissolved in benzene, extracted with 50% hydrochloric acid, washed with water, dried, and chromatographed on alumina to yield, after removal of the solvent, a polysulphide (4·8 g.) containing traces of unreacted sulphur (Found: C, 34·5; H, 4·55; N, 0·13%; C : H, 6 : 9·5). Infra-red analysis of this material revealed the presence of *cyclo*hexenyl groups, the spectrum closely resembling that of the polysulphide obtained from reaction of sulphur and *cyclo*hexene at 140°, and being different from those of the *cyclo*hexyl sulphides obtained from the diethylamine–sulphur–*cyclo*hexene reaction described above.

Synthesis of NN′-*Mono- and -Poly-thiobisdiethylamines*.—(1) The compound (VII), prepared according to Blake (*J. Amer. Chem. Soc.*, 1943, **65**, 1267), was obtained as a faintly yellow liquid, b. p. 78°/10 mm., n_D^{20} 1·4622 (73%) (Found : N, 15·9; S, 18·35. Calc. for $C_8H_{20}N_2S$: N, 15·9; S, 18·2%).

(2) The *NN′*-dithiobisamine, obtained from diethylamine and sulphur monochloride (purified by repeated distillation over sulphur under reduced pressure) according to Throdahl and Harman (*loc. cit.*), had b. p. 74·5°/0·05 mm., n_D^{20} 1·5132 (Found : N, 13·0; S, 30·6, 30·8. Calc. for $C_8H_{20}N_2S_2$: N, 13·4; S, 30·8%).

(3) The *NN′*-trithiobisamine (cf. Levi, *Gazzetta*, 1931, **61**, 286) was obtained as a light yellow liquid, b. p. 101·5—103·5°/0·3 mm., n_D^{22} 1·5428 (Found : N, 11·5; S, 39·3. Calc. for $C_8H_{20}N_2S_3$: N, 11·6; S, 40·0%). Infra-red analysis confirmed the absence of the above *NN′*-thioamines from the sulphur–amine–*cyclo*hexene reaction product.

Thermal Decomposition of NN′-*Monothiobisdiethylamine* (VII).—This compound (2·40 g.) was heated *in vacuo* at 140° ± 1° for 21 hr. The resulting dark brown liquid was distilled at 50 mm., and the distillate collected in a trap cooled in liquid air. The distillate contained diethylamine, characterised as its toluene-*p*-sulphonate, m. p. and mixed m. p. 58—59°. During the distillation diethylammonium hydrogen sulphide (VI) collected in the condenser. The residual liquid (1·50 g.) on distillation gave a main fraction, b. p. 50—54°/0·1 mm., n_D^{20} 1·5515 (Found : N, 12·3; S, 27·55%), shown by infra-red analysis to be mainly (IV), but additional bands at 839, 928, 1031, 1242, and 1282 cm.$^{-1}$ indicated a minor amount of (V). The formation of (IV) was further confirmed by the chemical methods described on p. 2085. An undistillable tar (0·80 g.) which remained from the above distillation was not further examined.

Reaction of (VII) *with* cyclo*Hexene*.—The compound (VII) (17·6 g., 0·1 mole) and the olefin (41·0 g., 0·5 mole) were heated *in vacuo* for 21 hr. at 140° ± 1°. Treatment of the product with ligroin, followed by filtration, afforded an insoluble tar together with crystalline (VI) from the main soluble material. The latter, after removal of volatile material, gave a product (11·5 g.) which on distillation gave : (i) b. p. ~70°/0·05 mm., n_D^{20} 1·5330 (1·0 g.) (Found : C, 59·8; H, 9·85; N, 8·25; S, 20·35%); (ii) b. p. 70—80°/0·05 mm., n_D^{20} 1·5352 (1·1 g.) (Found : C, 59·4; H, 9·9; N, 7·45; S, 22·3%); (iii) b. p. 80—85°/0·05 mm., n_D^{20} 1·5332 (0·6 g.) (Found : C, 65·1; H, 10·05; N, 5·05; S, 19·3%). Extensive decomposition set in at this stage and no further attempt was made to fractionate the residual tar (Found : N, 3·45; S, 27·3%). The infra-red spectra of (i)—(iii) were similar and showed the presence of di*cyclo*hexyl sulphides and (IV), and the absence of *cyclo*hexenyl groups and (VII).

In a second experiment, (VII) (10·0 g.) and *cyclo*hexene (20·0 g.) were heated for 16 hr. at 140° ± 1°. After separation of tar (1·0 g.), the liquid product was distilled at 20°/12 mm., and the distillate collected in a trap cooled in liquid air. Water was added to the distillate, and the mixture titrated with standard hydrochloric acid to estimate the diethylamine (Found : 5·29 g.). The *cyclo*hexene layer of this distillate was separated, washed, dried, and distilled to give the olefin, b. p. 82°/760 mm., n_D^{20} 1·4468, without a residue, thus confirming that the basic material was diethylamine and not unchanged (VII).

Reactions of N-*Ethylthioacetamide* (IV).—(1) *Action on* cyclo*hexene*. The olefin (5·0 g.) and

(IV) (3·15 g.), b. p. 70—72°/0·1 mm., n_D^{20} 1·5600, were heated *in vacuo* for 20 hr. at 140° ± 1°. The product consisted of unchanged olefin and a separate layer, b. p. 50—52°/0·02 mm., n_D^{20} 1·5601 (2·90 g.), which was shown by infra-red analysis to be unchanged (IV).

(2) *Separation from* cyclo*hexyl sulphides.* A mixture of *cyclo*hexyl sulphides and (IV), b. p. 96—100°/2 mm. (Found : N, 6·4%), was dissolved in ligroin (40 ml.) and extracted with cold 50% hydrochloric acid (2 × 30 ml.). The ligroin layer yielded on distillation a fraction, b. p. 93—97°/1 mm. (Found : N, 0·17%), the infra-red spectrum of which showed the absence of (IV).

(3) *Catalysis of thiol oxidation by sulphur.* Ethanethiol (8·4 g.) was mixed with sulphur (4·3 g.) and (IV) (0·1 g.) at room temperature. After a short induction period, hydrogen sulphide was evolved, and the product on fractionation gave a mixture of diethyl di- and polysulphides.

Non-reaction of Diethylamine with cyclo*Hexene.*—A mixture of the amine (3·0 g.) and olefin (5·0 g.) was heated *in vacuo* for 21 hr. at 140° ± 1°. On distillation of the product only unchanged reactants, b. p. 56—82°/760 mm. (7·2 g.), were isolated.

*Non-reaction of Di*cyclo*hexylamine with Dimethyl Disulphide at* 140°.—The amine (4·5 g., 0·025 mole) and the disulphide (2·35 g.; 0·025 mole; n_D^{20} 1·5200) were heated in pure nitrogen for 5 hr. at 140° ± 1°. Fractionation of the product gave unchanged disulphide, b. p. 104—108°/760 mm., n_D^{20} 1·5208, and amine, b. p. 118—120°/10 mm., n_D^{20} 1·4875. No dimethyl monosulphide was detectable.

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British Rubber Producers' Research Association,
48 Tewin Road, Welwyn Garden City, Herts.

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