582. *The Reactions of Amines and Sulphur with Olefins. Part IV.*[1] *The Chemical and Thermal Decompositions of* NN′-*Thiobisamines and Their Reactions with Olefins.*

By R. W. Saville.

NN′-Thiobisamines, $(RR'N)_2S_x$ ($x > 1$), undergo N–S bond fission in the presence of hydrogen sulphide, thiols, and other polar reagents. On thermal decomposition at 140° they give the parent amine, hydrogen sulphide, and thioamides, R·NH·CS·R″. *NN′*-Dithiobisdibenzylamine with *cyclo*hexene at 140° gives a complex mixture of mainly saturated sulphides and polymeric sulphides containing benzyl and *cyclo*hexyl groups, together with *N*-benzyl(thiobenzamide) and dibenzylamine. A novel method of olefinic sulphuration with the thiobisamines and hydrogen sulphide is described and the effect of the thiobisamines on interaction of sulphur and olefin is examined. Mechanisms of the thermal decomposition and of the reactions with olefins are discussed.

Parts I—III of this series[1] described the use of combinations of secondary amine and sulphur and of *NN′*-thiobisdiethylamine $Et_2N{\cdot}S{\cdot}NEt_2$ as olefinic sulphurating agents. The introduction[1] of *NN′*-thiobisamines, $(RR'N)_2S_x$, as vulcanising agents for rubber justifies a more detailed study of their properties.

Chemical Decomposition of NN′-*Thiobisamines*.—The reactivity of the N–S bond in sulphenamides, RR′N·SR″, with electrophilic reagents has been studied by several workers,[2] but little attention has been paid to the comparable reactivity of *NN′*-thiobisamines. Blake[3] showed that carbon disulphide and carbon oxysulphide caused N–S bond fission in the thiobisamines and led to thiuram sulphides, $(R_2N{\cdot}CS)_2S_x$, and thiocarbamoyl derivatives, respectively:

$$R_2N{\cdot}S_x{\cdot}NR_2 + 2CSX \longrightarrow R_2N{\cdot}C({:}X){\cdot}S_{x+2}{\cdot}C({:}X){\cdot}NR_2$$

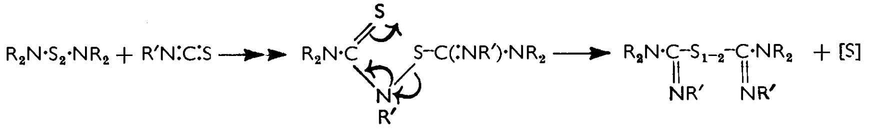
In dilute hydrochloric acid the thiobisamines liberate amine, presumably in the manner: $R_2N{\cdot}S_x{\cdot}NR_2 + 2HCl \longrightarrow 2R_2NH + S_xCl_2$, the sulphur halide then yielding sulphur, sulphur dioxide, and hydrogen sulphide.[4] Indicative of preferential N–S, rather than S–S, bond fission in dithiobisamines, $R_2N{\cdot}S_2{\cdot}NR_2$, is Lecher and Weigel's observation,[5] now confirmed, that sulphurous acid affords substances formulated as $[R_2NH^+]_2[S_2O_3H^-]_2$. Treatment in a solvent with hydrogen sulphide rapidly affords sulphur and the parent amine. Similar rapid fission of the N–S bond is observed in the reaction with thiols at room temperature, in the solid state or in ethanol solution, the amine and the tetrasulphide derivative from the thiol being formed in high yield:

$$(C_4H_8ON)_2S_2 + 2C_6H_4Me{\cdot}SH \longrightarrow 2C_4H_9ON + C_6H_4Me{\cdot}S_4{\cdot}C_6H_4Me$$

(C_4H_9ON = morpholine.)

This constitutes a new preparative method for organic tetrasulphides. Thiol-acids with thiobisamines, and thiols with sulphenamides, react similarly, and this is responsible for the catalytic action of thiols on rubber vulcanisation by accelerators containing N–S bonds.

Blake's work[3] has now been extended to *iso*thiocyanates: methyl and benzyl *iso*thiocyanate react readily with dithiobisamines:[6]



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[1] Parts I—III, Moore and Saville, *J.*, 1954, 2082, 2089; Glazebrook and Saville, *J.*, 1954, 2094.

[2] *E.g.*, Carr, Smith, and Alliger, *J. Org. Chem.*, 1949, **14**, 921; Chabrier and Renard, *Bull. Soc. chim. France*, 1950, **17**, D13.

[3] Blake, *J. Amer. Chem. Soc.*, 1943, **65**, 1267; U.S.P. 2,368,515/1945.

[4] Cf. Olin, *J. Amer. Chem. Soc.*, 1926, **48**, 167.

[5] Lecher and Weigel, G.P., 520,857/1927.

[6] Cf. Koch, *J.*, 1949, 401.

The effect of Friedel–Crafts catalysts on the N–S bond in thiobisamines has not been examined in detail, but Burg and Woodrow [7] found that boron trifluoride forms stable complexes, presumably by utilisation of the unshared electrons of the nitrogen. The reduction of *NN*-dithiobismorpholine with lithium aluminium hydride gives morpholine, hydrogen sulphide, and sulphur.

Thermal Decomposition of NN'-*Thiobisamines*.—*NN'*-Dithiobisdibenzylamine at 140° *in vacuo* gives dibenzylammonium hydrogen sulphide and *N*-benzyl(thiobenzamide), which are also formed by reaction of dibenzylamine with sulphur at 140° (cf. Moore and Saville [1]):

$$\mathrm{Ph{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}Ph + 2S \longrightarrow H_2S + Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}Ph}$$

Hydrogen sulphide and amine are also formed when *NN'*-dithiobis-(2-ethylaminopropionitrile) is heated at 140°, but in this case, and in the reaction of 2-ethylaminopropionitrile with sulphur at 140°, the expected thioamide could not be identified.

Thermal Reaction of NN'-*Thiobisamines with Olefins*.—Negligible reaction occurs between *NN'*-mono- or -di-thiobismorpholine and *cyclo*hexene or 2 : 6-dimethylocta-2 : 6-diene at 140°, in contrast to the extensive reaction [1] of *cyclo*hexene with *NN'*-monothiobisdiethylamine at 140°.

With *cyclo*hexene at 140° *NN'*-dithiobisdibenzylamine yields a complex mixture: (*a*) benzyl *cyclo*hexyl sulphide and mixed sulphides R_2S_x ($R = \mathrm{Ph{\cdot}CH_2}$, C_6H_{11}, C_6H_9; $x = 1$—2); (*b*) polymeric sulphides of the type $\mathrm{Ph{\cdot}CH_2{\cdot}S_x{\cdot}C_6H_{10}S_x{\cdot}CH_2{\cdot}Ph}$; (*c*) *N*-benzylthiobenzamide; (*d*) dibenzylamine; (*e*) *NN'*-trithiobisdibenzylamine; and (*f*) traces of benzylamine, benzaldehyde, and toluene. Considerable migration of benzyl groups occurs during the above reaction, as in reactions of other benzyl-substituted sulphur compounds, *e.g.*, benzyl alkyl xanthates and benzylsulphonium compounds,[8] and (benzylthio)benzothiazole,[9] and the smooth isomerisation of sulphidimines [8] fails with the dibenzyl compound, $\mathrm{(Ph{\cdot}CH_2)_2S{\cdot}N{\cdot}SO_2{\cdot}Ar}$. The monosulphide in fraction (*a*) was identified as its sulphone and by infrared spectroscopy, and the polysulphides in (*b*) by spectroscopy and by reduction with lithium aluminium hydride to toluene-ω-thiol in high yield, together with a polymeric monosulphide analogue and a *cyclo*hexanedithiol, of unknown composition, isolated as its bis-2 : 4-dinitrophenyl sulphide (minor amounts of *cyclo*hexane- and *cyclo*hex-2-ene-thiol were also isolated).

The formation of benzaldehyde, benzylamine, and toluene in the above reactions of *NN'*-dithiobisdibenzylamine is attributed to Willgerodt reactions of the type examined by King and McMillan,[10] and thioamide alkylation: [1]

$$\mathrm{Ph{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}Ph + (Ph{\cdot}CH_2)_2NH \longrightarrow Ph{\cdot}CH_2{\cdot}NH_2 + Ph{\cdot}CS{\cdot}N(CH_2{\cdot}Ph)_2}$$

followed by hydrogenolysis of benzyl groups of the amine.[11]

With 1-methyl*cyclo*hexene at 140° *NN'*-dithiobisdibenzylamine gives the thioamide and a high yield of dibenzylamine. The main product had a lower H : C ratio than that of the parent olefin, suggesting the presence of benzyl groups, and its infrared spectrum was consistent with the presence of benzyl 1-methyl*cyclo*hexyl sulphide and di-(1-methyl*cyclo*hexyl) sulphides. Presence of the former was confirmed by oxidation to the sulphone. Hydrogenolysis of the sulphuration product yielded toluene-ω-thiol in large amount, together with a small proportion of 1-methyl*cyclo*hexanethiol and di-(1-methyl*cyclo*hexyl) monosulphide; from the spectral data 2-methyl*cyclo*hexanethiol may also have been present, and the mechanistic significance of this is discussed below.

Olefinic Sulphuration with NN'-*Dithiobisamines and Hydrogen Sulphide*.—The ready interaction of hydrogen sulphide and thiols with *NN'*-dithiobisamines suggests a novel method of olefinic sulphuration. Reaction of 2-methylpent-2-ene with *NN'*-dithiobismorpholine at 20° and 65° was not effected by catalytic amounts of hydrogen sulphide but

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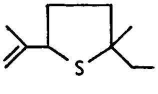
[7] Burg and Woodrow, *J. Amer. Chem. Soc.*, 1954, **76**, 219.

[8] Ash, Challenger, and Greenwood, *J.*, 1951, 1877; Ash and Challenger, *J.*, 1952, 2792.

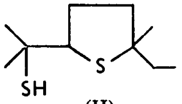
[9] Moore and Waight, *J.*, 1952, 4237.

[10] King and McMillan, *J. Amer. Chem. Soc.*, 1948, **70**, 4145.

required molar quantities of this agent, and then negligible sulphuration of the olefin occurred. Boiling *cyclo*hexene gave similar results. However, 2 : 6-dimethylocta-2 : 6-diene with *NN*′-dithiobismorpholine and hydrogen sulphide at 140° gave in 1 hour morpholine and a high yield of largely saturated, sulphurated product, in which the ratio of cross-linked polysulphide to cyclic sulphide was considerably greater than was observed for the comparable reaction with sulphur[12] or with sulphur and diethylamine.[1] No detailed analysis of the cyclic sulphide fraction was attempted but the presence of *ca.* 26% of the



(I)



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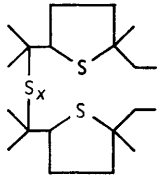
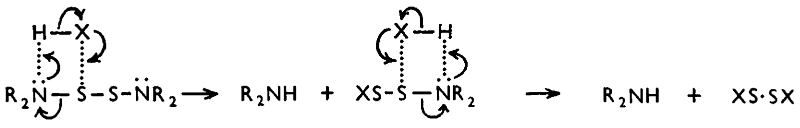


(III)

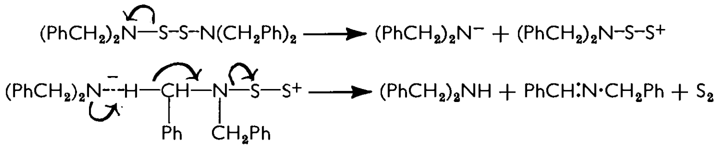
thiophan (I) was indicated by infrared spectroscopy. The polysulphide was mainly saturated, its infrared spectrum being similar to that of compound (II), suggesting that the polysulphide (III) was the major component as similarly obtained from the diene–sulphur–diethylamine reaction.[1] This was confirmed by hydrogenolysis of the polysulphide with lithium aluminium hydride, a thiol similar to (III) being obtained.

Mechanism of the Decomposition of NN′-*Dithiobisamines.*—The formation of amine (R_2NH) by reaction of *NN*′-dithiobisamines, $R_2N{\cdot}S_2{\cdot}NR_2$, with reagents of the type HX (X = Cl, SO_3H, SH, SR′) indicates that fission of the N–S bond is an important reaction of this type of compound, *e.g.*:



When HX is a thiol the products are amine and tetrasulphide, but when it is hydrogen sulphide the initially formed H_2S_4 probably forms the salt $R_2NH_2^+HS_4^-$ which decomposes further, particularly in a polar solvent or on treatment with acid, to give sulphur and $R_2NH_2^+HS^-$, as observed experimentally.

The thermal decomposition of *NN*′-dithiobisdibenzylamine to dibenzylamine, hydrogen sulphide, and *N*-benzyl(thiobenzamide) may be explained similarly as involving initial heterolysis of the N–S bond followed by elimination, thus:



Formation of hydrogen sulphide and *N*-benzylthiobenzamide is then regarded as resulting from (*a*) reaction of the dibenzylamine with sulphur (cf. Moore and Saville[1]), and (*b*) reaction of the benzylidenebenzylamine with sulphur. Although the presence of the Schiff's base in the products could not be proved support for its formation as an intermediate includes (i) the formation of thioamides from Schiff's bases and sulphur,[13] and (ii) the isolation of Schiff's bases in sulphur–amine reaction products.[14]

Isolation of *NN*′-trithiobisdibenzylamine on reaction of the dithiobisamine with *cyclo*hexene at 140° points to disproportionation involving S–S bond fission as an alternative

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[11] Hartung and Simonoff, " Organic Reactions," Wiley, New York, 1953, Vol. VII, p. 263.

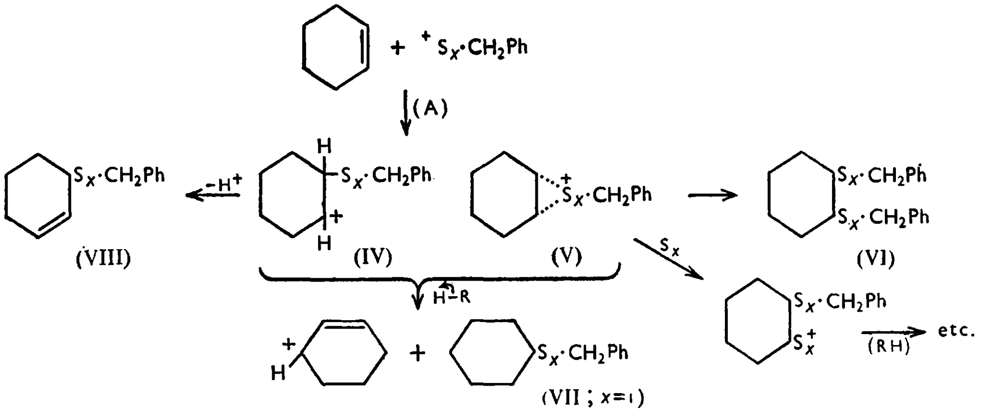
[12] Bateman, Glazebrook, and Moore, *J.*, 1958, 2846.

[13] Kindler, *Annalen*, 1923, **431**, 187; Böttcher and Bauer, *ibid.*, 1950, **568**, 218.

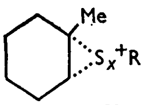
[14] Rosser and Ritter, *J. Amer. Chem. Soc.*, 1937, **59**, 2179.

to some extent to N–S fission. Comparable reactions have been observed with substituted thiuram disulphides, $R_2N{\cdot}CS{\cdot}S{\cdot}S{\cdot}CS{\cdot}NR_2$.

Mechanism of Olefinic Sulphuration with NN′-*Dithiobisdibenzylamine.*—Unlike the reaction of *NN′*-thiobisdiethylamine with *cyclo*hexene [1] that of *NN′*-dithiobisdibenzylamine with olefins yields products which result mainly from the addition of benzylthio-groups to olefinic double bonds, indicating an anomalous course for olefinic sulphuration. The reactions which lead to the formation of the benzylthio-groups remain obscure, but the observed products may result from the electrophilic attack of benzylthio- or benzylpolythio-cations, $Ph{\cdot}CH_2{\cdot}S_x^+$, on the olefin. Thus the major products obtained from *cyclo*hexene, *viz.*, benzyl *cyclo*hexyl sulphide and the polymer $Ph{\cdot}CH_2{\cdot}S_x{\cdot}C_6H_{10}{\cdot}S_x{\cdot}CH_2Ph$ (IV; x = mainly 1), may be formed as shown in the annexed scheme. The intermediate formed from the initial reaction (A) may be assigned either a classical cationic structure (IV) or a π-complex structure (V). Cyclic sulphonium ions of type (V) (cf. Bartlett and Swain [16]) were regarded by Lien, McCaulay, and Proell [17] as chain carriers for the formation of compounds analogous to the polysulphides (VI) in acid-catalysed reaction of disulphides with olefins, and participation of such intermediates in the present reaction is in conformity with recent mechanistic studies of olefin–sulphur reactions.[18] Formation of the monosulphide (VII) is represented as involving hydride-ion transfer between olefin and (IV—V),[18] which is well known in the analogous Friedel–Crafts reactions.[19] The isolation of a little *cyclo*hex-2-enethiol on hydrogenolysis of the polymeric fraction (*b*) (p. 2881) suggests that a polysulphide (VIII) may be a minor product, formed as shown.



The corresponding reaction of the dithiobisamine with 1-methyl*cyclo*hexene (p. 2881) recalls the isolation of 1-methyl*cyclo*hexyl phenyl sulphide on reaction of diphenyl tetrasulphide with 1-methyl*cyclo*hexene.[20] It is believed that these reactions follow the pattern suggested for *cyclo*hexene, proceeding *via* the intermediate sulphonium ion (IX) and leading mainly to tertiary C–S compounds.



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Mechanism of Olefinic Sulphuration with Dithiobismorpholine and Hydrogen Sulphide.—Since negligible reaction occurs at 140° between dithiobismorpholine and *cyclo*hexene or 2 : 6-dimethylocta-2 : 6-diene, the ready sulphuration of the diene in the presence of hydrogen sulphide must be due to reaction of the dithiobisamine with hydrogen sulphide.

[15] Craig, Juve, Davidson, Semon, and May, *J. Polymer Sci.*, 1952, **8**, 321.
[16] Bartlett and Swain, *J. Amer. Chem. Soc.*, 1949, **71**, 1406.
[17] Lien, McCaulay, and Proell, Amer. Chem. Soc., General Papers, Pet. Chem. Div., Sept. 1952, No. 28, p. 169.
[18] Bateman, Moore, and Porter, preceding paper.
[19] Baddeley and Pickles, *J.*, 1952, 3726.
[20] Bloomfield, *J.*, 1947, 1547.

The active sulphurating agent appears to be $C_4H_8ONH_2{}^+{\cdot}HS_4{}^-$ and the mechanism of sulphuration is probably analogous to that in the amine–sulphur–olefin systems.[1]

The formation of amines by reaction of hydrogen sulphide and thiols with dithiobisamines has been used to confirm the belief[21] that hydrogen sulphide and thiols are not intermediates in sulphur–olefin reactions. It was found that *cyclo*hexene and sulphur at 140° in the presence of dithiobismorpholine yield the normal olefinic polysulphide obtained also in the absence of the dithiobisamine and that morpholine formation is negligible.

EXPERIMENTAL

Preparation of NN′-*Dithiobisamines*.—NN′-*Dithiobisdibenzylamine*, obtained (92%) from dibenzylamine and sulphur monochloride by Throdahl and Harman's method,[22] crystallised from alcohol–light petroleum in pale yellow needles, m. p. 79—80° (Found: C, 73·5; H, 6·1; N, 6·05. $C_{28}H_{28}N_2S_2$ requires C, 73·7; H, 6·1; N, 6·1%). *NN*′-Dithiobismorpholine was obtained similarly (82%) as colourless needles [from ethanol–ethyl acetate (10 : 1)], m. p. 125° (Found: S, 27·0. Calc. for $C_8H_{16}O_2N_2S_2$: S, 27·1%). *NN*′-Dithiobis-(β-ethylaminopropionitrile) was obtained (66%) by Harman's method[23] as colourless prisms (from ethanol–acetone), m. p. 77—79° (Found: C, 46·8; H, 6·85; N, 21·2. Calc. for $C_{10}H_{18}N_4S_2$: C, 46·5; H, 7·0; N, 21·7%).

Preparation of Reference Compounds.—*N*-Benzyl(thiobenzamide), m. p. 84—85° (Found: C, 73·8; H, 5·75; N, 6·2. Calc. for $C_{14}H_{13}NS$: C, 74·0; H, 5·7; N, 6·2%), was prepared in 52% yield by reaction of *N*-benzylbenzamide (10 g.) with phosphorus pentasulphide (5 g.) in boiling xylene. It was recovered unchanged after 10 hr. at 140° *in vacuo*; it was not hydrolysed by dilute mineral acids, but in refluxing sulphuric acid (70% w/w) (1 hr.) gave benzoic acid, m. p. and mixed m. p. 120—121°, and benzylamine, isolated as the picrate, m. p. and mixed m. p. 193—194°.

cyclo*Hex-2-enethiol*, obtained (69%) from 3-bromo*cyclo*hexene and thiourea, had b. p. 44°/11 mm., n_D^{20} 1·5230 (Found: C, 63·65; H, 8·8; S, 27·35; SH, 28·4. $C_6H_{10}S$ requires C, 63·2; H, 8·8; S, 28·0; SH, 29·0%). It gave the 2 : 4-*dinitrophenyl derivative* as yellow prisms (from ethanol–acetone), m. p. 114—115° (Found: C, 51·55; H, 4·6; N, 10·05. $C_{12}H_{12}O_4N_2S$ requires C, 51·4; H, 4·3; N, 10·0%).

Thiophenol (11 g., 0·1 mole) was added with stirring to a solution of sodium (2·3 g., 0·1 g.-atom) in ethanol (40 ml.) under nitrogen, followed by 3-bromo*cyclo*hexene (16·1 g., 0·1 mole) in ethanol (15 ml.). After being warmed for 30 min. the mixture was poured into water, and extracted with ether, and the extract was washed with water, dried (K_2CO_3), and fractionated, to give *cyclo*hex-2-enyl phenyl sulphide, b. p. 89—90°/0·01 mm., n_D^{20} 1·5920 (79%) (Found: C, 75·35; H, 7·3; S, 16·65. Calc. for $C_{12}H_{14}S$: C, 75·8; H, 7·4; S, 16·8%).

Phenyl*cyclo*hexyl sulphide, b. p. 111°/0·1 mm., n_D^{20} 1·5680, was prepared by Cunneen's method.[24] The corresponding sulphone had m. p. 73—74°.

*cyclo*Hexene (15 g.), toluene-ω-thiol (30 g.), and ascaridole (0·1 g.) were refluxed on the steam-bath for 7 hr. and the product was fractionated, to give benzyl *cyclo*hexyl sulphide, b. p. 88—89°/0·01 mm., n_D^{22} 1·5556 (45%) (Found: C, 75·4; H, 8·7; S, 15·4. Calc. for $C_{13}H_{18}S$: C, 75·7; H, 8·7; S, 15·6%), which with peracetic acid gave the sulphone, colourless flakes from (ethanol–light petroleum), m. p. 100—101° (Found: C, 65·4; H, 7·55; S, 13·25. Calc. for $C_{13}H_{18}O_2S$: C, 65·5; H, 7·5; S, 13·4%).

Attempts to prepare 1 : 2-epithio*cyclo*hexane from 1-chloro-2-thiocyanato*cyclo*hexane and sodium sulphide[25] gave mainly a polymer, as expected for the alkaline conditions used,[26] and a thiol. Reduction of the polymer with lithium aluminium hydride gave the same thiol, b. p. 48—50°/0·1 mm., n_D^{20} 1·5410 (Found: C, 51·1; H, 8·25; S, 37·1. Calc. for $C_6H_{12}S_2$: C, 48·6; H, 8·1; S, 43·2%), which contained *cyclo*hexane-1 : 2-dithiol since on reaction with benzaldehyde and hydrogen chloride it gave the dithiolan,[27] m. p. 115°, and with potassium methyl

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[21] Ross, *J.*, 1958, 2856.
[22] Throdahl and Harman, *Ind. Eng. Chem.*, 1951, **43**, 421.
[23] Harman, U.S.P. 2,649,470; B.P. 708,627; B.P. 711,236.
[24] Cunneen, *J.*, 1947, 36.
[25] Farmer and Shipley, *J.*, 1947, 1519.
[26] Culvenor, Davies, and Heath, *J.*, 1949, 282.
[27] Cf. Culvenor and Davies, *Austral. J. Sci. Res.*, 1948, **1**, *A*, 236.

xanthate gave the *cyclo*hexyl trithiocarbonate,[28] m. p. 169°. Attempts to prepare a solid 2 : 4-dinitrophenyl sulphide derivative of the dithiol were unsuccessful.

Benzyl 1-methyl*cyclo*hexyl sulphide was prepared by Moore and Saville's method.[1] On oxidation with peracetic acid it gave the *sulphone* as flakes [from light petroleum–ethanol (10 : 1)], m. p. 100° (Found: C, 67·1; H, 8·0; S, 12·6. $C_{14}H_{20}O_2S$ requires C, 66·7; H, 7·9; S, 12·7%).

Chemical Decompositions of NN′-*Dithiobisamines.*—*NN*′-Dithiobisdibenzylamine (2·0 g.) was shaken vigorously with 15% sulphurous acid (50 ml.) and then cooled to 0° for 2 days. The S_4-*compound* separated (2·7 g.) and formed colourless prisms, m. p. 143—144°, from ethanol (Found: C, 53·55; H, 5·0; N, 4·25; S, 20·45. $C_{28}H_{32}N_2O_6S_4$ requires C, 54·2; H, 5·15; N, 4·5; S, 20·7%).

The same *NN*′-dithiobisamine was decomposed by warm dilute mineral acids to sulphur, hydrogen sulphide, sulphur dioxide, and the parent amine, identified as picrate.

A benzene solution of the *NN*′-dithiobisamine with hydrogen sulphide gave a red insoluble oil and sulphur; the decomposition was favoured by the presence of polar solvents.

NN′-Dithiobismorpholine (11·8 g., 0·05 mole) and toluene-*p*-thiol (12·4 g., 0·1 mole) were mixed as fine powders at room temperature: a rapid reaction ensued, the mixture becoming yellow, liquid, and finally deep red, with the evolution of a small amount of hydrogen sulphide. After 3 hr. the product was fractionated to give morpholine (5·8 g.), b. p. 25—30°/10 mm., n_D^{20} 1·4560 (identified as picrate, m. p. 146—147°), and a residual yellow oil (14·9 g.), undistillable at 140°/0·01 mm., which was devoid of thiol and appeared to be principally di-*p*-tolyl tetrasulphide (13·2 g.) (Found: C, 53·05; H, 4·7; S, 40·65. Calc. for $C_{14}H_{14}S_4$: C, 54·2; H, 4·5; S, 41·3%). Use of a solvent (*e.g.*, ethanol) gave a more controllable reaction and minimised side reactions leading to hydrogen sulphide. Other thiols reacted similarly. Comparable reactions between sulphenamides and thiols were less vigorous owing to the intermediate formation of the solid amine–thiol salt.

NN′-Dithiobisdibenzylamine (9·1 g., 0·02 mole) was unchanged when refluxed for 2 hr. with lithium aluminium hydride (1·9 g., 0·05 mole) in ether (200 ml.). The *NN*′-dithiobisamine (9·1 g.) in tetrahydrofuran (20 ml.) was then refluxed for 4 hr. with the reagent (3·0 g.) in tetrahydrofuran (50 ml.). Decomposition with ice and 2N-sulphuric acid gave hydrogen sulphide and a white solid (apparently dibenzylammonium sulphate) which was treated with alkali to yield dibenzylamine, isolated as its hydrochloride (4·5 g. equiv. to 3·8 g. of amine). The original ether extract gave only impure sulphur ($\ngtr$0·8 g.). The starting material was stable to cold 2N-sulphuric acid.

[With Dr. G. H. THOMAS].—(i) A mixture of *NN*′-dithiobismorpholine (3·0 g.) and methyl *iso*thiocyanate (2·5 g.) in benzene (20 ml.) was heated *in vacuo* for 8 hr. at 140°, giving sulphur and *di*-(α-*methylimino*-α-*morpholinomethyl*) *sulphide*, prisms (from ethanol), m. p. 150—151° Found: C, 50·45; H, 7·9; N, 20·0; S, 11·55. $C_{12}H_{22}O_2N_4S$ requires C, 50·3; H, 7·7; N, 19·6; S, 11·2%). (ii) A comparable reaction to (*i*), with benzyl *iso*thiocyanate, gave *di*-(α-*benzylimino*-α-*morpholinomethyl*) *disulphide*, plates (from benzene), m. p. 98° (Found: C, 61·1; H, 6·8; N, 11·95; S, 13·35. $C_{24}H_{30}O_2N_4S_2$ requires C, 61·3; H, 6·4; N, 11·9; S, 13·6%).

Thermal Decomposition of NN′-*Dithiobisdibenzylamine.*—(i) When this compound, m. p. 80°, was heated under nitrogen for 5 hr. at 140° no hydrogen sulphide was evolved and the product (Found: C, 73·55; H, 6·15%) had m. p. and mixed m. p. with the original compound, 70—71°, indicating possible disproportionation. (ii) The dithiobisamine (5·0 g.) was heated *in vacuo* for 20 hr. at 140° ± 1°: hydrogen sulphide was formed, together with *N*-benzyl(thiobenzamide) (2·1 g.), m. p. 83—84° (Found: C, 74·2; H, 6·1; N, 6·2. Calc. for $C_{14}H_{13}NS$: C, 74·0; H, 5·7; N, 6·2%). (iii) The dithiobisamine (9·1 g.) was heated in nitrogen for 24 hr. at 140° ± 1°, then treated in ether with hydrogen chloride, to give dibenzylammonium hydrochloride. Evaporation of the solution gave *N*-benzyl(thiobenzamide) (6·1 g.), m. p. 81—83° (Found: C, 74·1; H, 5·7; N, 6·2%).

Reaction of Dibenzylamine with Sulphur.—The amine (10·3 g.) and sulphur (2·0 g.) were heated *in vacuo* for 24 hr. at 140° ± 1° with shaking, then cooled to −10° for 2 days. *N*-Benzylthiobenzamide (4·2 g.), m. p. and mixed m. p. 84—85° (Found: C, 73·7; H, 5·9; N, 6·4%), separated. Evaporation of the filtrate gave dibenzylammonium hydrogen sulphide, m. p. (sealed tube) 32—34° (cf. Achterhof [29]).

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[28] Culvenor, Davies, and Pausacker, *J.*, **1946**, 1050.

[29] Achterhof, *J. Amer. Chem. Soc.*, 1931, **53**, 2687.

Thermal Decomposition of NN′-*Dithiobis*-(α-*ethylaminopropionitrile*).—Heating the compound *in vacuo* for 10 hr. at 140° ± 1° gave traces of the hydrogen sulphide of β-ethylaminopropionitrile and a tar.

Reaction of α-*Ethylaminopropionitrile with Sulphur.*—Heating the amine (9·8 g.) with sulphur (3·2 g.) *in vacuo* for 10 hr. at 140° ± 1° gave the amine hydrogen sulphide and tar.

Reaction of NN′-*Dithiobisdibenzylamine with* cyclo*Hexene.*—(1) The dithiobisamine (34·2 g., 0·075 mole) and the olefin (61·5 g., 0·75 mole) were heated *in vacuo* for 24 hr. at 140° ± 1°. The red-brown liquid yielded no crystals at −10° (1 week). Unchanged olefin (36 g.) was removed and to the residue was added light petroleum (250 ml.). A dark oil (∼5 g.) separated, which crystallised at low temperature, the solid product being *N*-benzyl(thiobenzamide), obtained as light yellow needles on repeated crystallisation (charcoal) from aqueous ethanol (m. p. and mixed m. p. 82—83·5°) (Found: C, 73·5; H, 5·75; N, 6·1%). Treatment of the petroleum solution with 2N-hydrochloric acid (150 ml.) gave dibenzylammonium hydrochloride (12·0 g.). This was removed, and the filtrate re-extracted with acid, washed with water, dried ($CaCl_2$), and evaporated, to give the olefinic sulphuration product (i) (33 g.) (Found: C, 72·65; H, 7·55; N, 1·3%; C : H, 6 : 7·5). Fractional distillation of this gave (ii) 2 : 4-dinitrotoluene, m. p. 70° (*ca.* 1 g.), (iii) a liquid, b. p. 88°/0·001 mm., n_{D}^{20} 1·5500 (5·7 g.) (Found: C, 73·7; H, 9·0; N, 0·07; S, 17·15%), and (iv) a deep red oil (15·3 g.), undistillable at 140°/0·001 mm. (Found: C, 71·0; H, 6·85; N, 1·89%) which at 0° slowly deposited a trace of *N*-benzyl(thiobenzamide).

Infrared spectroscopic analysis of fraction (iii) showed that the principal constituent (70%) was benzyl *cyclo*hexyl sulphide, by comparison with a synthetic sample. Refractionation gave (iii*a*) b. p. 78—80°/0·01 mm., n_{D}^{20} 1·5470 (4·0 g.) (Found: C, 74·0; H, 9·25; S, 16·2%; C : H, 6 : 9), and (iii*b*) b. p. 82—86°/0·01 mm., n_{D}^{20} 1·5665 (0·8 g.) (Found: C, 71·35; H, 8·65; S, 19·6%; C : H, 6 : 8·7). Infrared analysis of fractions (iii*a* and *b*) revealed benzyl *cyclo*hexyl sulphide as the main component, only small amounts of di*cyclo*hexyl and di*cyclo*hex-2-enyl sulphide being present. The presence of benzaldehyde in fractions (iii) and (iii*a* and *b*) was established by a band at 1710 cm.$^{-1}$ due to C=O in their infrared spectra, and by formation of benzaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 234—235°. Oxidation of fraction (iii) with peracetic acid gave benzyl *cyclo*hexyl sulphone, m. p. and mixed m. p. 100—101° (Found: C, 65·3; H, 7·55; S, 13·6. Calc. for $C_{13}H_{18}O_2S$: C, 65·5; H, 7·5; S, 13·4%). No other crystalline sulphone could be identified.

Extraction of a benzene solution of fraction (iv) with 10% sulphurous acid failed to give any S_4-derivative, indicating the absence of the dithiobisamine. [In an independent experiment, treatment of a benzene solution of the dithiobisamine with 10% sulphurous acid gave the S_4-compound (93%).] The benzene solution of fraction (iv) was washed with aqueous sodium hydrogen carbonate, then with water, dried, and eluted through alumina, to give fraction (v) (Found: C, 66·9; H, 6·15; N, 1·8; S, 25·2%; C : H, 6 : 6·6). A solution of this fraction (14·0 g.) was refluxed with stirring with lithium aluminium hydride (5·0 g.) in ether (250 ml.) for 2 hr., then decomposed with ice and 2N-sulphuric acid. Removal of the solvent and fractionation gave: (v*a*) impure *cyclo*hex-2-enethiol, b. p. 40°/10 mm., n_{D}^{25} 1·5070 (0·5 g.) (Found: C, 62·75; H, 9·2; S, 26·6; SH, 28·8%; C : H, 6 : 10·5. Calc. for $C_6H_{10}S$: C, 63·2; H, 8·8; S, 28·0; SH, 29·0%) (its infrared spectrum indicated >40% of the thiol; it gave 2 : 4-dinitrophenyl *cyclo*hex-2-enyl sulphide (m. p. 115°, mixed m. p. 114—115°); (v*b*) b. p. 60—80°/10 mm., n_{D}^{25} 1·5460 (2·1 g.) (Found: C, 65·8; H, 7·6; S, 25·35%; C : H, 6 : 8·4) [shown by infrared analysis to contain toluene-ω-thiol (70%) identified as its 2 : 4-dinitrophenyl derivative, m. p. and mixed m. p. 128—129° (Found: C, 53·4; H, 3·45; N, 9·4. Calc. for $C_{13}H_{10}O_4N_2S$: C, 53·8; H, 3·45; N, 9·7%); the presence of *cyclo*hexanethiol was demonstrated by the formation of 2 : 4-dinitrophenyl *cyclo*hexyl sulphide, m. p. and mixed m. p. 145·5—147°]; (v*c*) b. p. 35°/0·01 mm., n_{D}^{25} 1·5645 (1·1 g.) (Found: C, 59·65; H, 7·4; S, 32·25%; C : H, 6 : 8·9) [shown by infrared analysis to consist mainly of benzyl *cyclo*hexyl sulphide (or material of the type $Ph{\cdot}CH_2{\cdot}S{\cdot}C_6H_{10}{\cdot}S{\cdot}CH_2Ph$) together with toluene-ω-thiol, identified as the 2 : 4-dinitrophenyl derivative, m. p. and mixed m. p. 125—127° (Found: C, 53·45; H, 3·5; N, 9·8%), and a *cyclo*hexanedithiol of unknown composition characterised as its bis-2 : 4-dinitrophenyl derivative, m. p. 193—194·5° (Found: C, 45·5; H, 3·45; N, 11·35. Calc. for $C_{18}H_{16}O_8N_4S_2$: C, 45·1; H, 3·34; N, 11·7%)]; (v*d*), b. p. 84—88°/0·01 mm., n_{D}^{25} 1·5590 (0·65 g.) (Found: C, 69·1; H, 8·4; S, 21·8%; C : H, 6 : 8·7) [shown by infrared analysis to be mainly benzyl *cyclo*hexyl sulphide and $Ph{\cdot}CH_2{\cdot}S{\cdot}C_6H_{10}{\cdot}S{\cdot}CH_2Ph$, but containing also a *cyclo*hexanedithiol characterised as its bis-2 : 4-dinitrophenyl derivative, m. p. 195—196°]; and (v*e*) a residue (7·8 g.) undistillable at 140°/0·001 mm. Chromatography of (v*e*) (7·0 g.) in light petroleum gave (v*f*) a light yellow oil (1·8 g.) [Found: C, 74·1; H, 7·65; N, 1·35%; C : H, 6 : 7·4; *M* (ebullioscopic in C_6H_6), 294, 303)], and further elution with light petroleum–ethanol (19 : 1) gave (v*g*) a yellow oil (4·0 g.] [Found: C, 78·75; H, 7·35; N, 3·0%; C : H, 6 : 7; *M* (as above), 362, 372]. Infrared examination of fractions (v*f* and *g*) indicated the presence of benzyl and *cyclo*hexyl groups suggestive of the presence of $Ph{\cdot}CH_2{\cdot}S{\cdot}C_6H_{10}{\cdot}S{\cdot}CH_2Ph$ and apparently traces of *N*-benzyl-(thiobenzamide), but definitely precluded the presence of tetrabenzylhydrazine.

(2) Reaction of *NN'*-dithiobisdibenzylamine (22·8 g.) with *cyclo*hexene as above gave a fraction (0·65 g.) which was almost pure benzylamine, b. p. 35°/0·2 mm., n_D^{20} 1·5425 (Found: C, 78·15; H, 8·4; N, 12·5; S, 1·0. Calc. for C_7H_9N: C, 78·5; H, 8·4; N, 13·0%), identified as its picrate, m. p. 198—199° (Found: C, 46·25; H, 3·5; N, 16·9. Calc. for $C_{13}H_{12}O_7N_4$: C, 46·4; H, 3·6; N, 16·7%).

(3) The dithiobisamine (17·1 g.) and olefin (36·9 g.) were heated *in vacuo* for 10 hr. at 140° ± 1°. The product, which contained no tar, was freed from volatile material, and the residue (20·7 g.) cooled to 0°: it partially crystallised. Filtration gave a solid (10·1 g.) which crystallised from light petroleum (charcoal) in prisms, m. p. 72—73° (Found: C, 71·05; H, 5·8; N, 5·65%). Fractionation from light petroleum then gave NN'-*trithiobisdibenzylamine* as prisms (from light petroleum or ethanol–ethyl acetate), m. p. 109—111° (Found: C, 68·85; H, 5·7; N, 5·37; S, 19·5. $C_{28}H_{28}N_2S_3$ requires C, 68·8; H, 5·7; N, 5·7; S, 19·7%). Examination of the more soluble fractions failed to yield any *NN'*-monothiobisdibenzylamine.

Reaction of NN'-*Dithiobisdibenzylamine with* 1-*Methyl*cyclo*hexene.*—A similar procedure to that followed in the *cyclo*hexene reaction was used. The main experimental findings are summarised on p. 2881.

Formation of Morpholine from 2-*Methylpent*-2-*ene*, NN'-*Dithiobismorpholine, and Hydrogen Sulphide.—General Procedure.* The *NN'*-dithiobisamine (5·9 g., 0·025 mole) and the olefin (0·25 mole) were stirred rapidly at 20° or 65° for 1 hr. while either a trace or a steady stream of hydrogen sulphide was introduced. After removal of solid *NN'*-dithiobisamine and/or sulphur, the solution was freed from olefin and the residue fractionated or titrated directly in aqueous ethanol against standard hydrochloric acid to determine the yield of morpholine (identified as its picrate) (see Table). In two control experiments the olefin was replaced by ethanol and by light petroleum.

Expt. no.	1	2	3	4	5	6	7
Olefin	†	†	†	0	0	†	†
H_2S	0	Tr	†	†	†	Tr	†
Temp.	65°	65°	65°	65°	65°	20°	20°
Other solvent	—	—	—	Pet	EtOH	—	—
Yield (g.) of morpholine	0·0	0·1	2·8	0·67	1·3	0·4	0·4
NN'-Dithiobisamine recovered (g.)	5·6	5·45	—	—	—	—	—

† = Excess. Tr = trace. Pet = light petroleum.

Reaction of 2 : 6-*Dimethylocta*-2 : 6-*diene with* NN'-*Dithiobismorpholine in Absence and in Presence of Hydrogen Sulphide.*—(1) The olefin (25·0 g.) and the dithiobisamine (12·6 g.), refluxed under nitrogen for 1 hr. at 140°, gave a reddish-brown product, with no indications of amine hydrogen sulphide or of hydrogen sulphide formation. On cooling, unchanged dithiobisamine (8·8 g.) separated. Filtration and washing the filtrate with ice-cold light petroleum gave further dithiobisamine (1·8 g., total 85%).

(2) A stirred mixture of the olefin (25·0 g.) and the dithiobisamine (12·6 g.) was refluxed under nitrogen at 140° and hydrogen sulphide introduced during 1 hr. Morpholine hydrogen sulphide separated. The reddish-brown product was decanted from tar (2 g.) and fractionated to give fractions: (i) b. p. 36—50°/10 mm., n_D^{20} 1·4525 (6·5 g.) (Found: C, 54·9; H, 10·9; N, 11·43%), containing morpholine (picrate, m. p. 146—147°); (ii) b. p. 60—80°/10 mm., n_D^{20} 1·4535 (16·8 g.) (Found: C, 86·75; H, 10·85; N, 1·35%; C : H, 10 : 18), unchanged olefin containing a little morpholine (picrate, m. p. 146—147°); (iii) unchanged olefin plus cyclic sulphide, b. p. 89—92°/10 mm., n_D^{20} 1·4870 (0·9 g.) (Found: C, 77·0; H, 11·5; N, 0·07%; C : H, 10 : 18); (iv) evaporative distillate (1·7 g.) (Found: C, 56·1; H, 8·4; N, 0%; C : H, 10 : 18); (v) residue (5·0 g.) which on elution in benzene through alumina and removal of solvent gave a polysulphide (Found: C, 49·4; H, 7·45; N, 0·01%; C : H, 10 : 18). Infrared analysis confirmed the presence of morpholine and unchanged olefin in fractions (i) and (ii) and revealed the

presence of ~26% of $CH_2{:}CRR'$ in (iii) indicative of the cyclic sulphide; fraction (iv) contained $R{\cdot}CH{:}CRR'$ groups (band at 830 cm.$^{-1}$) but the major polysulphide fraction (v) was saturated (compound III). Fraction (v) showed no absorption maximum near 4000 Å, the absorption being consistent with that of a saturated polysulphide. A portion (4·0 g.) of fraction (v) in ether was reduced with lithium aluminium hydride (1·5 g.) in the usual manner and the product fractionated to give materials: (v*a*) b. p. 60°/0·1 mm., n_D^{20} 1·5110 (0·7 g.) (Found: C, 61·8; H, 10·1; S, 27·5; SH, 20·3%; C : H, 10 : 19·6); (v*b*) b. p. 78—80°/0·1 mm., n_D^{20} 1·5275 (0·9 g.) (Found: C, 56·85; H, 9·45; S, 28·9; H, 25·2%; C : H, 10 : 20); and (v*c*), a residue, which on elution in light petroleum (b. p. 40—60°) through alumina gave a polysulphide as an orange-red oil (Found: C, 58·05; H, 9·6; S, 28·8; C : H, 10 : 19·8. Calc. for $C_{20}H_{40}S_4$: C, 58·8; H, 9·8; S, 31·4%). The infrared spectra of (v*a* and *b*) showed strong resemblances to that of the thiol-cyclic sulphide (II), (v*a*) containing also traces of unsaturated material; the infrared spectrum of (v*c*) was similar to those of (v*a* and *b*).

Influence of NN′-*Dithiobismorpholine on the Sulphur*–cyclo*Hexene Reaction*.—*cyclo*Hexene (41 g., 0·5 mole), sulphur (4·8 g., 0·15 g.-atom), and the dithiobisamine (11·8 g., 0·05 mole) were heated *in vacuo* for 5 hr. at 140° ± 1°. The deep red liquid product was decanted from tar (1 g.) and fractionated to give: (i) impure morpholine, b. p. 40°/10 mm., n_D^{20} 1·4600 (0·6 g.) (Found: C, 56·3; H, 10·6; N, 14·4. Calc. for C_4H_9ON: C, 55·2; H, 10·35; N, 16·1%; (ii) dithiobisamine, b. p. 60°/0·001 mm. (1·2 g.); and (iii) a residue (16 g.) which was extracted from benzene, with 0·1N-hydrochloric acid, washed with water, extracted with sulphurous acid, washed, dried, eluted through alumina, and fractionated to give a polysulphide (10·5 g.) containing a trace of the dithiobisamine (Found: C, 53·45; H, 7·0; N, 0·5%; C : H, 6 : 9·4).

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