

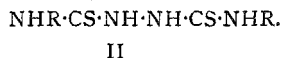
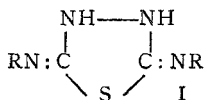
## II.—ACTION OF SULPHUR MONOCHLORIDE ON MERCAPTANS. PART III.

### OXIDATION OF UNSYMMETRICALLY SUBSTITUTED HYDRAZODITHIODICARBONAMIDES TO THIODIAZOLES.

By P. P. Patel and G. C. Chakravarti.

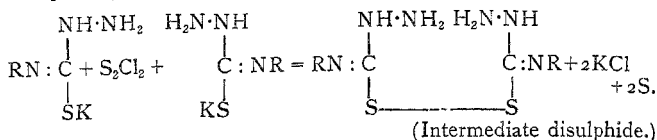
Having discussed in the previous communication, the action of sulphur monochloride on mercaptans, it seemed interesting to ascertain its effect on 'potential' mercaptans. Chakravarti (*J. C. S.*, 1923, 123, 964) stated that sulphur monochloride is capable of distinguishing real mercaptans from potential mercaptans, thus attributing to it a property resembling that ascribed to chloropicrin by Rây and Das (*J. C. S.*, 1922, 121, 323). Chakravarti's view was based on the partial or complete separation of sulphur when potential mercaptans react with sulphur monochloride, no separation occurring in the case of real mercaptans; he acted upon potential mercaptans, e.g., thio-benzoic acid and thiocarbamide with sulphur monochloride and in some cases identified the products.

A typical class of potential mercaptans was chosen, for besides the confirmation of the rule observed by Chakravarti, an interesting condensation giving rise to more definite products was anticipated. It is well known that 4-substituted thiosemicarbazides of the general formula,  $\text{NHR}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}_2$ , like thiocarbamides, in their aqueous or alcoholic alkaline solutions react in the tautomeric form,  $\text{NHR}\cdot\text{C}(\text{SH})\cdot\text{N}\cdot\text{NH}_2$ , or  $\text{NR}\cdot\text{C}(\text{SH})\cdot\text{NH}\cdot\text{NH}_2$ , and for this the work of Guha and Sen (*J. Indian Chem. Soc.* 1927, 4, 43) bears ample evidence. When, therefore, sulphur monochloride is allowed to react, at low temperatures, with such tautomeric forms of 4-substituted thiosemicarbazides condensation takes place and generally thiodiazoles (I) are formed along with small quantities of the corresponding hydrazodithiocarbamide derivatives (II):

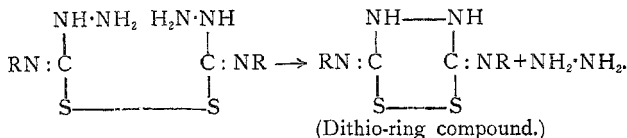


With respect to the mechanism of condensation, it is suggested that the first stage consists in the union of two molecules of the

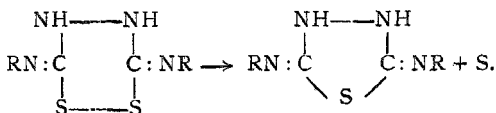
potassium salt of the thiosemicarbazide at the mercaptanic groups, with liberation of potassium chloride and formation of an intermediate disulphide (not isolated) thus :—



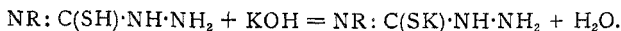
The disulphide then, under the conditions suitable for ring closure, is converted into another intermediate compound (a dithio-ring structure) with elimination of hydrazine as follows :—



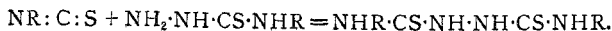
The dithio-ring compound, like disulphides with adjacent double bonds, decomposes with separation of sulphur (Cf. From, Layer and Ners, *Annalen*, 1923, **433**, 1) to yield the thioiazole (I) thus :—



The formation of the hydrazodithiodicarbonamide derivative (II) follows the partial decomposition of the thiosemicarbazide into hydrazine and mustard oil. While preparing the potassium derivative of the thiosemicarbazide by adding the latter to the calculated quantity of absolute alcoholic potash, a certain amount of water is formed as under :—



The water thus formed reacts partially with sulphur monochloride used in the reaction and produces hydrogen chloride, which even at ordinary temperature can decompose such thiosemicarbazides into hydrazine and the corresponding mustard oil, the latter uniting with unchanged thiosemicarbazide to produce (II) :—



We have substantial evidences in support of the above mechanism. Firstly, the formation of mustard oil has been observed, and secondly, the yield of II varies directly with the temperature of the reaction, within certain limitations. In a freezing mixture of ice and salt, the formation of II was altogether checked, the only product being I, while at room-temperature, II was the only product. Moreover, in every experiment at low temperatures, the mustard oil was found to have been formed. These observations show that when the temperature is sufficiently low, though slight decomposition into the mustard oil and hydrazine takes place, reaction of the mustard oil with the thiosemicarbazide does not occur, but that at comparatively higher temperatures decomposition proceeds to the formation of II.

That hydrochloric acid is responsible for changing the thiosemicarbazide to the hydrazodithiodicarbonamide derivative was confirmed by an independent experiment. When a small quantity of 4-phenylthiosemicarbazide was heated for a short time with dilute alcoholic hydrochloric acid solution, sparingly soluble *Sym*-diphenylhydrazodithiodicarbonamide was precipitated. In this connection it should be pointed out that the conclusion of Pulvermacher (*Ber.*, 1893, **26**, 2812; *ibid.*, 1894, **27**, 613) that phenylthiocarbamide is formed by the action of hydrogen chloride on 4-phenylthiosemicarbazide, seems doubtful.

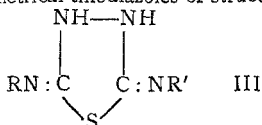
The action of sulphur monochloride on 4-phenyl, 4-*p*-tolyl- and 4-*o*-tolylthiosemicarbazides has been studied and the products described. With 4-phenylthiosemicarbazide under different conditions interesting results were not obtained. On slowly adding the agent in chloroform to a solution of 4-phenylthiosemicarbazide in the same solvent probably an unstable double compound was formed, giving sulphur and phenyl thiosemicarbazide hydrochloride on treatment with alcohol or water. A very small quantity of *Sym*-diphenylhydrazodithiodicarbonamide also separated.

The reaction with disubstituted thiosemicarbazides was also tried, but with little success. When sulphur monochloride in benzene was added to the tautomeric form of 1:4-phenyl-*p*-tolylthiosemicarbazide (stable, m.p. 176°), obtained by dissolving the thiosemicarbazide in a calculated quantity of potash, much decomposition occurred with formation of tar. If the reaction was conducted in chloroform without alcoholic potash, copious fumes of hydrogen chloride were evolved and the only product was a snuff coloured amorphous substance (of a high indefinite m.p.) precipitated by xylene from the pyridine solution of the crude product.

From 1:4-diphenylthiosemicarbazide an amorphous product free from sulphur, m.p. above 200° and having nitrogen 17.6 per cent, was

obtained by carrying out the reaction under similar conditions. Thus with 1:4-disubstituted thiosemicarbazides, unlike 4-monosubstituted, the reaction is complicated and the amorphous products may not even be ring compounds, but open chain compounds of very high molecular weight, as shown by their high melting points. The diminished basicity of 1:4-disubstituted thiosemicarbazides having a negative group like phenyl in the 1-position may be responsible for preventing ring closure (cf. Guha, *J. Amer. Chem. Soc.*, 1922, 44, 1502).

Unsymmetrical thiodiazoles of structure,



however, are not known: it appeared likely that these might also be obtained by the action of mild oxidising agents on dissimilarly substituted hydrazodithiocarbonamides of the general formula,  $\text{NHR} \cdot \text{CS} \cdot \text{NH} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHR}'$ . Only one such carbonamide has been prepared by From, Soffner and Frey (*Annalen*, 1923, 434, 285). In the course of this investigation several similar derivatives have been prepared and converted into thiodiazoles of the general formula III, by the action of iodine; these, like I and II, also form diacetyl derivatives. During study of this reaction it was observed that boiling pyridine converts all 1, 6-disubstituted hydrazodithiocarbonamides into the corresponding thiodiazoles.

## EXPERIMENTAL

*Interaction of the Potassium Derivative of 4-Phenylthiosemicarbazide and Sulphur Monochloride. Formation of 2:5-Diphenyldi-imino-2:3:4:5-tetrahydro-1:3:4-thiodiazole and Sym-Diphenylhydrazodithiocarbonamide.*

4-Phenylthiosemicarbazide (6 g.) was dissolved in 25 c.c. of absolute alcoholic potash containing 8.036 g. per 100 c.c. and while stirred a solution of sulphur monochloride (3 g.) in 25 c.c. of dry benzene was gradually added; an orange colour changing to yellowish white developed. Stirring was continued for 15 minutes more and the liquid filtered through a fluted paper was pink. The residue was washed on the paper three times with hot absolute alcohol and the collected filtrates concentrated to one-third yielded on cooling a small amount of solid; on crystallisation from boiling alcohol or pyridine diluted with water it melted at 184° with effervescence (Found: C, 55.58; H, 4.45; N, 19.27; S, 21.16.  $\text{C}_{14}\text{H}_{14}\text{N}_4\text{S}_2$  requires C, 56.00;

H, 4.00; N, 18.66; S, 21.33 per cent.). The compound is easily soluble in dilute alkalis and readily loses sulphur when treated with iodine in a suitable solvent; it is identical with *Sym*-diphenylhydrazodithiocarbonamide.

The mother liquor was further concentrated and cooled, yielding a solid which crystallised from alcohol or dilute acetone in lustrous plates, m.p. 247° (Found: C, 62.75; H, 4.21; N, 19.8; S, 12.2.  $C_{14}H_{12}N_4S$  requires C, 62.70; H, 4.47; N, 20.8; S, 11.9 per cent.). The compound was identified with 2,5-diphenylimino-2:3:4:5-tetrahydro-1:3:4-thiodiazole (Guha, *J. Amer. Chem. Soc.*, 1923, 45, 1036); From, Layer and Nerz (*loc. cit.*), however, give 243° while Busch and Schmidt (*Ber.*, 1913, 46, 2240) give 240° as the m.p. of the thiodiazole. The substance is soluble in hot alcohol, acetone, pyridine, but sparingly in ether and chloroform. The *diacetyl* derivative from acetic anhydride was crystallised from alcohol and melted at 225° (Found: N, 16.68.  $C_{18}H_{16}O_2N_4S$  requires N, 16.00 per cent.).

#### 4-*p*-Tolythiosemicarbazide and Sulphur Monochloride.

4-*p*-Tolythiosemicarbazide from *p*-tolyl mustard oil and hydrazine hydrate melts at 139–140° after several crystallisations from alcohol; Guha and Ray (*J. Amer. Chem. Soc.*, 1925, 47, 385) give 172°, while Busch and Ulmer (*Ber.*, 1902, 35, 1744) obtaining it by an indirect method give 134–135°.

4-*p*-Tolythiosemicarbazide (6.5 g.) was dissolved in 25 c.c. of the specified alcoholic potash and treated with sulphur monochloride (3 g.) in 25 c.c. of dry benzene; *sym*-di-*p*-tolylhydrazodithiocarbonamide was one of the products and melts at 198° with gas evolution (Found: N, 16.4; S, 19.0.  $C_{16}H_{18}N_4S_2$  requires N, 17.0; S, 19.9 per cent.).

2:5-Di-*p*-tolyl-di-imino-2:3:4:5-tetrahydro-1:3:4-thiodiazole was separated from the above hydrazo-compound by the procedure adopted previously, and after crystallisation from alcohol melts at 248° (Found: N, 18.56; S, 10.98.  $C_{16}H_{16}N_4S$  requires N, 18.91; S, 10.81 per cent.). The *diacetyl* derivative melts at 172° (Found: N, 15.25.  $C_{20}H_{20}O_2N_4S$  requires N, 15.13 per cent.), but Guha (*loc. cit.*) gives 235°.

#### 4-*o*-Tolythiosemicarbazide and Sulphur Monochloride.

With 4-*o*-tolythiosemicarbazide (m.p. 145°) the reaction gave two products which were separated as already described; *sym*-Di-*o*-tolylhydrazodithiocarbonamide melts at 175°, From, Soffner and Frey (*Annalen*, 1923, 434, 285) giving 179° (Found: N, 17.3; S, 19.72.  $C_{16}H_{18}N_4S_2$  requires N, 17.0; S, 19.9 per cent.). The second product,

2 : 5-di-*o*-tolyl-di-imino-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, crystallises from alcohol and melts at 222°, and appears to be new (Found: N, 18·86; S, 10·25.  $C_{15}H_{16}N_4S$  requires N, 18·91; S, 10·81 per cent.).

The *diacetyl* derivative crystallises from alcohol and melts at 257° (Found: N, 1505.  $C_{20}H_{20}O_2N_4S$  requires N, 15·13 per cent.).

*4-Phenylthiosemicarbazide and Sulphur Monochloride at varying Temperatures.*

(a) *In a freezing mixture.*—A solution of 4-phenylthiosemicarbazide (6 g.) in 25 c.c. of the specified alcoholic potash was cooled in the freezing mixture while stirred, and a solution of sulphur monochloride (3 g.) in anhydrous benzene admitted drop by drop. When the reaction seemed completed, the pink solution was filtered from sulphur and potassium chloride. After washing the solid several times with alcohol the collected filtrates were concentrated and cooled in a freezing mixture, when a white solid separated and crystallised from alcohol in plates melting at 247°; a second crop had the same m.p.

(b) *At 27°.*—An almost quantitative yield of *sym*-diphenylhydrazodithiodicarbonamide, m.p. 184°, was obtained without a trace of the thiodiazole.

*Action of boiling Pyridine on sym-Diphenylhydrazodithiodicarbonamide.*

The hydrazo-compound dissolved in boiling pyridine gave a clear solution which on cooling deposited much less solid than was originally taken, and was found to be unchanged substance. On cooling the mother liquor with ice nothing separated, but dilution with water gave a precipitate which, when recrystallised from alcohol, melted at 246° and was found to be 2 : 5-diphenyldiimino-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole.

*4-Phenylthiosemicarbazide and Sulphur Monochloride in Chloroform.*

4-Phenylthiosemicarbazide (16·7 g.) heated under reflux with 600 c.c. of dried chloroform gave an almost clear solution; to this was added a solution of sulphur monochloride (6·75 g.) in 25 c.c. of dry chloroform, with shaking, and allowed to remain for some time with a calcium chloride guard-tube. The faint yellow solution was then filtered from about 9–10 grams of 4-phenylthiosemicarbazide hydrochloride, and after most of the solvent was distilled, there remained a thick oil smelling of phenyl mustard oil; treatment with ether gave *sym*-diphenylhydrazodithiodicarbonamide melting at 184°.

2 : 5-*Phenyl-o-tolyldiimino*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole*.

4-Phenylthiosemicarbazide and *o*-tolyl mustard oil (molecular proportion) in boiling alcohol gave 1 : 6-phenyl-*o*-tolylhydrazodithiodicarbonamide which, crystallised from dilute pyridine, melts at 179°. The oxidation was conducted according to the method of From, Layer and Nerz (*loc. cit.*), an alcoholic solution of iodine being added in small portions to 1 : 6-phenyl-*o*-tolylhydrazodithiodicarbonamide (7 g.) in 80 c.c. of 95 per cent. boiling alcohol under reflux. Addition of iodine was stopped when a permanently brown and almost clear solution was obtained. The filtrate from sulphur gave a copious white precipitate of the thiodiazole with caustic potash and this when crystallised from 95 per cent. alcohol melts at 200° (Found : N, 20.5.  $C_{15}H_{14}N_4S$  requires N, 19.9 per cent.). The *diacetyl* derivative was crystallised from alcohol, m. p. 223° (Found : N, 15.92.  $C_{19}H_{18}O_2N_4S$  requires N, 15.3 per cent.).

2 : 5-*Phenyl-m-tolyldiimino*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole*.

1 : 6-Phenyl-*m*-tolylhydrazodithiodicarbonamide prepared from 4-phenylthiosemicarbazide and *m*-tolyl mustard oil melts at 180°. The thiodiazole obtained from this by oxidation as described in the last case melts at 216°, when crystallised from alcohol (Found : N, 20.3.  $C_{15}H_{14}N_4S$  requires N, 19.9 per cent.). The *diacetyl* derivative crystallised from alcohol melts at 177° (Found : N, 15.69.  $C_{19}H_{18}O_2N_4S$  requires N, 15.3 per cent.).

2 : 5-*Tolyl-m-tolyldiimino*-2 : 3 : 4 : 5-*tetrahydro* 1 : 3 : 4-*thiodiazole*.

1 : 6-*o*-Tolyl-*m*-tolylhydrazodithiodicarbonamide prepared from 4-*o*-tolylthiosemicarbazide and *m*-tolyl mustard oil melts at 166°. The thiodiazole obtained by oxidation melts at 190° when crystallised from alcohol; the *diacetyl* derivative melts at 231° (Found : N, 14.75.  $C_{20}H_{20}O_2N_4S$  requires N, 14.73 per cent.).

2 : 5-*m-Xylyl-m-tolyldiimino*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole*.

1 : 6-*m*-Xylyl-*m*-tolylhydrazodithiodicarbonamide prepared from 4-*m*-xylylthiosemicarbazide (m.p. 142°) and *m*-tolyl mustard oil melts at 161°. The thiodiazole obtained by oxidation melts at 190°; the *diacetyl* derivative melts at 263° (Found : N, 13.93.  $C_{21}H_{22}O_2N_4S$  requires N, 14.21 per cent.).

2 : 5-*o-Tolyl-m-xylyldiimino* 2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole*.

1 : 6-*o*-Tolyl-*m*-xylylhydrazodithiodicarbonamide obtained from 4-*o*-tolylthiosemicarbazide and *m*-xylyl mustard oil (b.p. 258°), melts at

164°. The thiodiazole crystallises from alcohol and melts at 205°; the *diacetyl derivative* melts at 224° (Found: N, 14.33.  $C_{21}H_{22}O_2N_4S$  requires N, 14.21 per cent.).

2 : 5-Phenyl-*m*-xylyldiimino-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole.

1:6-Phenyl-*m*-xylylhydrazodithiodicarbonamide from 4-phenylthiosemicarbazide and *m*-xylyl mustard oil melts at 171°. The thiodiazole crystallised from alcohol melts at 189°; the *diacetyl derivative* crystallised from alcohol melts at 120° (Found: N, 14.73.  $C_{20}H_{20}O_2N_4S$  requires N, 14.73 per cent.).

### SUMMARY.

Interaction of sulphur monochloride and 4-substituted thiosemicarbazides gives thiodiazoles along with small quantities of hydrazodithiodicarbonamides.

Several new mixed hydrazodithiodicarbonamides have been prepared and oxidised to the corresponding thiodiazoles.

Pyridine has been found to act as a ring closing agent on hydrazodithiodicarbonamide and its derivatives.

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