

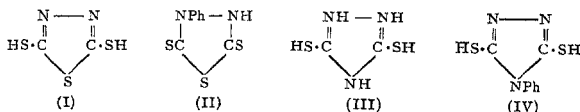
CONSTITUTION OF THE SO-CALLED DITHIO-URAZOLE OF MARTIN FREUND.

PART XI. ISOMERIC CHANGES OF SOME TRIAZOLES AND THIOBIAZOLES.

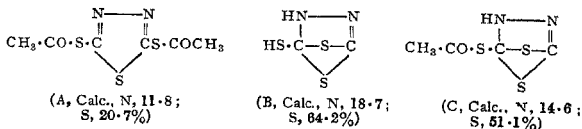
By P. C. Guha and S. L. Janniah.

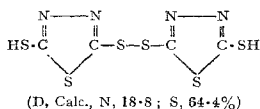
The discrepancy observed in the melting points and sometimes even in other properties of compounds in the triazole and thiobiazole series formed from hydrazodithiodicarbonamide and its substituted compounds suggested the existence of different isomeric forms of the same substance and this has been amply justified by the successful isolation (*cf.* preceding parts) of the isomeric varieties of a number of substances of this class, as also by the determination of the exact experimental conditions under which the isomers are formed.

At this stage, it was considered desirable to extend the work further by way of examining the action of acetic anhydride upon some dithiotriazoles and thiobiazoles, with a view to studying whether these compounds undergo transformation to give rise to isomeric compounds possessing endo-structures. The four compounds, *viz.*, 3:5-dithiol-4:1:2-thiobiazole (I), 3:5-dithio-1-phenyl-tetrahydro-4:1:2-thiobiazole (II), 3:5-dithiol-4:1:2-triazole (III) (dithio-urazole), 3:5-dithiol-4-phenyl-4:1:2-triazole (IV), have hence been subjected to the action of acetic anhydride and concentrated hydrochloric acid.



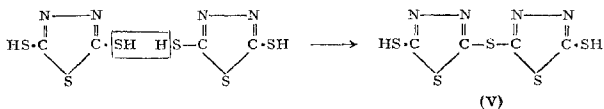
3:5-Dithiol-4:1:2-thiobiazole (I), when treated with acetic anhydride gave a deep yellow compound melting with decomposition at 180° C. and on analysis gave N, 20.93 and S, 58.3 per cent. These values do not agree with those of any of the compounds (A, P, C, D).





The observed values do not agree even with those of the di-acetyl derivative of D (Calc., N, 14.7; S, 50.3 per cent.). The mean of three independent determinations of molecular weight by the method of Rast (*Ber.*, 1922, 55, 1051, 3737) gave a value of 258. This can only be the case if the substance possesses the structure (V) with a molecular weight of 266, and a percentage composition of nitrogen and sulphur (N, 21.05; S, 60.10 per cent.) closely agreeing with the values found.

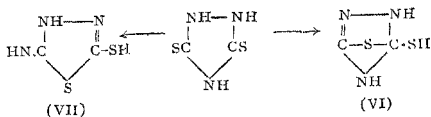
A careful study of the mode of formation of endo-thio compounds by the action of acetic anhydride, as well as of concentrated hydrochloric acid, on imino-thiobiazolone and imino-thiol-thiobiazole will, however, reveal the fact that the transformation of the compound V from (I) is not anomalous. Instead of an intramolecular bridge formation (as in the case of the endo-compounds) acetic anhydride has effected, in the present instance, an inter-molecular bridge formation by eliminating one molecule of hydrogen sulphide from two molecules of dithiolthiobiazole, thus,



The dibenzyl derivative obtained from the above substance (V) fully confirmed the presence of two mercaptanic groups.

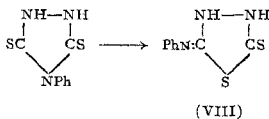
1-Phenyl-3-thio-5-thiol-4:1:2-thiobiazole on being similarly treated with acetic anhydride remains unchanged. In this substance there is only one thiol-group; the other sulphur atom being unable to exhibit mercaptanic properties for want of another labile hydrogen atom. Perhaps, this is the reason why the substance remained unaffected.

Dithiourazole (III), m.p. 196°, on being treated with acetic anhydride gave a diacetyl derivative, m.p. 330° (decomp.). This on being deacetylated by means of concentrated hydrochloric acid gave a yellow substance melting at 228° (decomp.) and was found to be identical in chemical composition to the original dithioltriazole. This can either be the endo-thio-triazole (VI) (in analogy with the substances described in the previous parts) or the iminothiolthiobiazole (VII) formed by the interchange of positions between sulphur and the imino-group, thus,

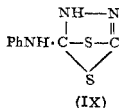


The value for the molecular weight of the substance, m.p. 228° , was found to be near about 140—close to the molecular weight (133) of the parent triazole itself.

That such an intramolecular change or displacement can be effected by means of concentrated hydrochloric acid is only to be expected from a consideration of the observations made by Arndt (*Ber.*, 1922, 55, 341; 1923, 56, 2276). Conclusive proof about this sort of intramolecular rearrangement has been obtained in the case of 4-phenyl-3:5-dithio-4:1:2-triazole (m.p. 216°), which when boiled with concentrated hydrochloric acid gives two substances, one soluble in alkali and the other insoluble. The former had the same chemical composition as that of the original triazole, namely, $\text{C}_8\text{H}_7\text{N}_3\text{S}_2$ and melted sharply at 219° , and has been proved to be identical with 3-thio-5-phenylimino-tetrahydro-4:1:2-thiobiazole (VIII). This definitely establishes the formation of a thiobiazole from a triazole compound, and this can happen only if the sulphur atom from one of the thioketo groups exchanges position with the phenylimino group of position 4, thus,



The other substance, insoluble in alkali, formed in the reaction decomposes at 260° and is likely to be an endo compound of the structure (IX).



Formation of the phenyliminothiobiazole (VIII) from phenyldithio-urazole suggests, however, that the compound (m.p. 228°) obtained from dithiourazole is likely to be imino-thiol-dihydro-thiobiazole (VII) which, it has been shown in Part IV, can exist in two isomeric forms.

EXPERIMENTAL.

*Dithiol-thiobiazole and acetic anhydride: Formation of (V).—*The thiobiazole (3.8 g.) prepared according to the method of Busch (*Ber.*, 1894, 27, 2519) on being warmed with acetic anhydride (15 c.c.) soon dissolved and the solution was then gently boiled for about five minutes and immediately cooled. A small quantity of water was added to the solution until it became turbid, and then allowed to stand overnight. Next day, the separated deep yellow solid was filtered, well pressed, and washed thoroughly with water and dilute alcohol. It was insoluble in alcohol, ether, chloroform, and acetic acid, and melted between 173–176°. It was then purified by dissolving in cold 2N sodium hydroxide solution and precipitating with hydrochloric acid and the pale yellow solid thus obtained melted sharply at 180°. On further crystallisation, the melting point remained unchanged (Found: N, 20.93; S, 59.3; Mol. Wt., 257, 253, 264. $C_4H_2N_4S_5$ requires N, 21.05; S, 60.1 per cent.; Mol. Wt., 266).

The Dibenzyl-derivative.—The above substance (1 mol., 3 g.) dissolved in excess of 2N potassium hydroxide solution, was heated under reflux with benzyl chloride (2 mol., 3 g.) dissolved in dilute alcohol for about half-an-hour. A white shining, crystalline solid separated on cooling and crystallised from dilute alcohol, m.p. 107° (Found: N, 12.8; S, 34.3. $C_{18}H_{14}N_4S_5$ requires N, 12.5; S, 35.8 per cent.).

3:5-Dithiol-triazole and acetic anhydride: Formation of (VI) or (VII).—The triazole prepared from hydrazine hydrate and perthiocyanic acid according to the method of Fromm (*Annalen*, 1922, 426, 313) was gently warmed with acetic anhydride in which it dissolved readily. The pale yellow solution was heated to boiling and then allowed to cool. On the addition of a few drops of water, the solution became turbid and was allowed to stand overnight. Next day, the separated acetyl derivative was filtered, washed and dried, m.p. with decomp. 330° (Found: N, 18.96; S, 30.01. $C_6H_7O_2N_3S_2$ requires N, 19.35; S, 29.5 per cent.).

Hydrolysis of the acetyl derivative.—The acetyl derivative obtained above was boiled with concentrated hydrochloric acid for a few minutes and the solution allowed to cool. A pale yellow solid separated which was filtered, washed and crystallised from water, m.p. 228° (Found: N, 31.13; S, 48.6. $C_2H_8N_3S_2$ requires N, 31.58; S, 48.1 per cent.).

4-Phenyl-3:5-dithiol-1:3:4-triazole and hydrochloric acid.—The triazole compound (3 g.), prepared according to the method of Arndt (*Ber.*, 1922, 55, 341), was treated with concentrated hydrochloric acid in the usual way when a dirty white solid was thrown

out of the solution first formed. This melted within a wide range of temperature, *vis.*, 200–240°. It was then shaken with dilute caustic soda solution in which a portion appeared to dissolve leaving a small quantity insoluble. The insoluble portion after filtration and washing melted at 260° with decomposition and could not be further examined the yield being very poor. The alkaline filtrate on acidification gave a pale yellow crystalline solid, m.p. 217–219°. It crystallised from dilute alcohol in pale yellow needles, m.p. 219°; mixed melting point with a genuine sample of 3-thio-5-phenylimino-tetrahydro-4:1:2-thio-biazole (m.p. 219°) remained undepressed (Found: S, 30.55. $C_8H_7N_2S_2$ requires S, 30.62 per cent.).

SUMMARY.

3:5-Dithiol-4:1:2-thiobiazole on treatment with acetic anhydride gives the sulphide of 3-thiol-4:1:2-thiobiazole. In the case of 3:5-dithiol-1:2:4-triazoles an interchange of position between one of the sulphur atoms of the thioketo groups and the imino-group of position 4, takes place. Thiobiazoles substituted in position 1 or 2 do not undergo any change.

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