III.—*Oxidation of Benzalthiosemicarbazone.*

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It has been shown by Marckwald (*Ber.*, 1892, **25**, 3098; 1899, **32**, 1081) that certain thiosemicarbazides, for example,

exist in two forms, of which the labile modification when treated with phosgene yields a mercaptotriazole, whilst the stable form with the same reagent yields an aminothiodiazolone. This difference, Marckwald ascribes to stereoisomerism, thus :

Young and Witham having found that benzalsemicarbazone could be oxidised by ferric chloride to phenylhydroxytriazole (*Trans.*, 1900, **77**, 224),

we thought it might be of interest to apply the same reaction to benzalthiosemicarbazone in order to determine, if possible, whether this compound would act as a mixture, or as one or the other of the two possible stereoisomeric forms :

The substance represented by formula I would yield an aminophenylthiodiazole, III, whilst that represented by II would yield a phenylmercaptotriazole, IV.

The oxidation of benzalthiosemicarbazone by ferric chloride takes place much more easily than that of benzalsemicarbazone; the latter requires to be heated with an alcoholic solution of ferric chloride in sealed tubes at 130—140°, whereas the thio-compound is oxidised by aqueous ferric chloride between 70° and 80°. The product consists almost entirely of the hydrochloride of a base which has the properties to be expected of an aminothiodiazole. In one or two experiments, there was also obtained a trace of a substance of high melting point and soluble in alkali, which may have been the mer-

captotriazole, but the quantity obtained was too small to admit of purification. Benzalthiosemicarbazone reacts, therefore, with ferric chloride almost, if not entirely, as if it had the constitution represented by formula I. Changes in the conditions under which the oxidation took place produced no effect on the nature of the product.

We endeavoured, but without success, to obtain a second form of benzalthiosemicarbazone.

Our results being negative do not preclude the possibility of a second form, but, on the other hand, the substance may be tautomeric, and might, with another oxidising agent, yield the mercaptotriazole in the same manner as, according to Marckwald and Bott (*Ber.*, 1896, 29, 2914), benzoyl-4-phenylthiosemicarbazide yields phenylamino-phenylthiodiazole when treated with acetyl chloride, but diphenylmercaptotriazole when acted on by excess of benzoyl chloride, or when heated above its melting point,

Benzal-4-phenylthiosemicarbazone and benzal-4-methylthiosemicarbazone undergo oxidation by ferric chloride to the corresponding phenylamino- and methylamino-phenylthiodiazole :

Traumann (*Annalen*, 1889, 249, 53) showed that the aminothiazoles can be equally well represented as iminothiazolines :

Gabriel (*Ber.*, 1889, 22, 1144 ; 1898, 31, 2832) found the amino-thiazolines, $\begin{array}{c} \text{H}_2\text{C} \cdot \text{N} \\ \parallel \\ \text{H}_2\text{C} - \text{S} \end{array} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C} \cdot \text{NH}_2$, to react sometimes as such, sometimes as the tautomeric form, $\begin{array}{c} \text{H}_2\text{C} \cdot \text{NH} \\ \parallel \\ \text{H}_2\text{C} - \text{S} \end{array} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C} : \text{NH}.$

The aminothiodiazoles discussed in this paper are very similar in structure to the above compounds, and although we make use, as far as possible, of the "amino" nomenclature and constitutional formulæ, the reactions and properties of our substances might be represented just as well by the "imino" constitution.

The structure of the methyl and acetyl derivatives of aminophenylthiodiazole is of some interest in connection with the work of Pulvermacher and of Freund on the aminothiodiazoles.

Pulvermacher (*Ber.*, 1894, 27, 613) found that phenylaminothi-di-

azole on methylation and subsequent decomposition yielded aniline and methylamine, and he therefore gave to the base, the methyl derivative, and the acetyl derivative the respective formulæ :

Freund and Meinecke (*Ber.*, 1896, **29**, 2511) methylated aminothiodiazole and aminomethylthiodiazole, and by comparison with the corresponding synthetical bases prepared by Pulvermacher, determined the constitution of the methyl derivatives to be

and, following Pulvermacher's example, assumed that the acetyl derivatives were similarly constituted :

Aminophenylthiodiazole yields with methyl iodide a methyl derivative which is isomeric, and not identical with the methylaminophenylthiodiazole which we have prepared by the oxidation of benzal-4-methylthiosemicarbazone :

To the methyl base prepared by methylation and to its acetyl derivative, we must ascribe the constitutional formulæ :

Aminophenylthiodiazole yields with acetic anhydride an acetyl derivative which has distinctly acid properties. It is easily soluble in dilute alkalis, and forms stable sodium and silver derivatives. The action of methyl iodide on the silver acetyl compound yields a methyl acetyl derivative which is identical with the above acetyl derivative of the methylated aminophenylthiodiazole. The acetyl derivative of aminophenylthiodiazole must therefore have the constitution

We consider that there is no ground for the assumption that the methyl and acetyl groups take up the same position when an aminothiodiazole is methylated or acetylated, and as our acetylaminophenylthiodiazole closely resembles the acetyl derivatives described by Freund

and Meinecke, we are of opinion that the constitution which they ascribe to these acetyl compounds is open to doubt, and that their substances would be better represented by the formulæ :

The acetyl derivative of methylaminophenylthiodiazole has probably the constitution :

EXPERIMENTAL.

Benzalthiosemicarbazone, $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{N} \cdot \text{N} : \text{C}(\text{SH}) \cdot \text{NH}_2$.—Thiosemicarbazide, prepared according to the method described by Freund and Imgart (*Ber.*, 1895, 28, 948), was dissolved in warm alcohol and benzaldehyde added. On cooling, part of the benzalthiosemicarbazone crystallised out in hair-like needles, and the remainder was precipitated by the addition of water.

Benzalthiosemicarbazone is easily soluble in warm alcohol, and slightly so in boiling water, from which it crystallised, on cooling, in long, thin, shining plates which melted at 156° . After recrystallisation from alcohol, the substance melted at 159 — 160° .

Benzalthiosemicarbazone has slightly acid properties, as it is fairly soluble in caustic soda, and is reprecipitated by dilute hydrochloric acid.

0.2140 gave 0.2716 BaSO_4 . $\text{S} = 17.41$.

$\text{C}_8\text{H}_9\text{N}_3\text{S}$ requires $\text{S} = 17.87$ per cent.

Benzalthiosemicarbazone is easily oxidised by aqueous ferric chloride. The oxidation commences at about 70° . The best results were obtained by suspending the benzalthiosemicarbazone in water, adding rather more than one molecular proportion of ferric chloride, and warming for half an hour in a water-bath at 80 — 90° . After filtering from a small amount of solid matter A, the filtrate was slightly concentrated, if necessary, and allowed to cool.

The hydrochloride of the oxidation product crystallised out in white needles which, after recrystallisation, melted at 213 — 214° . Further quantities of less pure hydrochloride were obtained by concentrating the mother liquors.

The hydrochloride contains one molecular proportion of water of crystallisation, which is given off at 90° .

0.2904 gave 0.1810 AgCl . $\text{HCl} = 15.86$.

0.5172, at 90° , lost 0.0420 H_2O . $\text{H}_2\text{O} = 8.12$.

0.3312, dried at 90° , gave 0.2182 AgCl . $\text{HCl} = 16.76$.

$\text{C}_8\text{H}_7\text{N}_3\text{S} \cdot \text{HCl} \cdot \text{H}_2\text{O}$ requires $\text{HCl} = 15.76$; $\text{H}_2\text{O} = 7.77$ per cent.

$\text{C}_8\text{H}_7\text{N}_3\text{S} \cdot \text{HCl}$ requires $\text{HCl} = 17.10$ per cent.

The solid matter, A, consisted principally of unchanged benzalthiosemicarbazone, but in some experiments contained also a very small amount of a substance of higher melting point which was soluble in alkalis. This substance, which was not further investigated, may have been the mercaptotriazole isomeric with the base which formed the chief product.

Aminophenylthiodiazole, $C_6H_5 \cdot C \begin{smallmatrix} \text{N} \cdot \text{N} \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{NH}_2$.—The hydrochloride obtained by the oxidation of benzalthiosemicarbazone was dissolved in water and excess of ammonia added. The precipitated base on recrystallisation from 50 per cent. alcohol, formed colourless, microscopic hexagonal plates which melted at 222—223°.

0.2148 gave 0.4294 CO_2 and 0.0800 H_2O . $\text{C} = 54.52$; $\text{H} = 4.14$.

0.2570 „ 55 c.c. moist nitrogen at 23° and 755.2 mm. $\text{N} = 23.96$.

0.2456 „ 0.3194 BaSO_4 . $\text{S} = 17.83$.

$C_8H_7N_3S$ requires $\text{C} = 54.24$; $\text{H} = 3.95$; $\text{N} = 23.72$; $\text{S} = 18.08$ per cent.

The base is easily soluble in dilute acids. On addition of concentrated hydrochloric acid to the solution in dilute acid, the hydrochloride described above is obtained.

Acetylaminophenylthiodiazole, $C_6H_5 \cdot C \begin{smallmatrix} \text{N} \cdot \text{N} \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_3$.—The base was added to an equal weight of acetic anhydride. The mixture rapidly became hot and soon solidified. The product on recrystallisation from boiling alcohol formed small needles which melted at 276°.

0.3052 gave 0.3214 BaSO_4 . $\text{S} = 14.44$.

$C_{10}H_9ON_3S$ requires $\text{S} = 14.61$, per cent.

The acetyl compound is very slightly soluble in water, moderately so in boiling alcohol, and easily so in aqueous alkalis. A sodium derivative is precipitated by the addition of concentrated aqueous caustic soda to the solution in the dilute alkali.

The silver derivative was prepared by dissolving the acetyl compound in dilute ammonia and running the solution into aqueous silver nitrate. The white precipitate was washed with water and alcohol.

0.1742 gave 0.0576 Ag . $\text{Ag} = 33.07$.

$C_{10}H_9ON_3S\text{Ag}$ requires $\text{Ag} = 33.13$ per cent.

Acetylaminomethylphenylthiodiazoline,

—The silver acetyl derivative was treated with methyl iodide and methyl alcohol, and after standing overnight was heated for half an

hour at 100° in a sealed tube. The product, recrystallised from boiling alcohol, formed prismatic needles melting at 144°.

0.2378 gave 37.7 c.c. moist nitrogen at 14° and 751.2 mm. N = 18.43.

0.2578 „ 0.2534 BaSO₄. S = 13.48.

C₁₁H₁₁ON₃S requires N = 18.03 ; S = 13.73 per cent.

Iminomethylphenylthiodiazoline, $\text{C}_6\text{H}_5 \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{N} (\text{CH}_3) \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{NH} \cdot \text{—}$

Aminophenylthiodiazole was heated with methyl iodide and methyl alcohol in a sealed tube for 1 hour at 100°. On cooling, the hydriodide of the new base crystallised out in large, flat prisms which melted at 245—246°. On addition of aqueous caustic potash to the hydriodide, the base separated as an oil. The hydrochloride melts at 218—219°, and the platinichloride at 217—218°. On analysis of the latter :

0.3134 gave 0.0776 Pt. Pt = 24.76

(C₉H₉N₃S)₂, H₂PtCl₆ requires Pt = 24.62 per cent.

On adding the base to acetic anhydride heat was developed and on cooling the acetyl derivative crystallised out. This compound has the same melting point (144°) and crystalline appearance as the acetylmino-methylphenylthiodiazoline described above. It was analysed with the following result :

0.1410 gave 22.4 c.c. moist nitrogen at 16.5° and 744.2 mm. N = 18.08.

C₁₁H₁₁ON₃S requires N = 18.03 per cent.

Benzal-4-methylthiosemicarbazone, C₆H₅·CH·N·N·C(SH)·NH·CH₃, was prepared according to Pulvermacher's directions (*Ber.*, 1894, 27, 623) and its properties agreed with his description.

0.1368 gave 26.2 c.c. moist nitrogen at 16° and 740.0 mm. N = 21.72.

C₉H₉N₃S requires N = 21.76 per cent.

This compound was oxidised with ferric chloride in exactly the same way as benzalthiosemicarbazone. The hydrochloride which separated was treated with aqueous caustic potash and the base thus obtained was crystallised from alcohol.

Methylaminophenylthiodiazole, $\text{C}_6\text{H}_5 \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{N} \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{NH} \cdot \text{CH}_3$, is

moderately soluble in hot alcohol, from which it separates in shining plates melting at 183—184°; it is fairly soluble in benzene, from which it crystallises in flat needles, and very slightly soluble in hot water from which it is deposited in microscopic, rough needles.

0.0950 gave 18.3 c.c. moist nitrogen at 15° and 744.2 mm. N = 22.07.

C₉H₉N₃S requires N = 21.99 per cent.

From the hydrochloride a platinichloride was prepared which melted at 208—209°.

0.5526 gave 0.1352 Pt. Pt = 24.46.

$(C_9H_9N_3S)_2, H_2PtCl_6$ requires Pt = 24.62 per cent.

Methylacetylaminophenylthiodiazole, $C_6H_5 \cdot C \begin{smallmatrix} N \cdot N \\ \diagup \quad \diagdown \\ S \end{smallmatrix} C \cdot N \begin{smallmatrix} CH_3 \\ \diagup \quad \diagdown \\ CO \cdot CH_3 \end{smallmatrix} \cdot -$

Methylaminothiodiazole was added to an excess of acetic anhydride. The acetyl compound crystallised from alcohol in long needles which melted at 195°.

0.1314 gave 20.6 c.c. moist nitrogen at 15° and 744.2 mm. N = 17.99.

$C_{11}H_{11}ON_3S$ requires N = 18.03 per cent.

Benzal-4-phenylthiosemicarbazone, $C_6H_5 \cdot CH:N:N:C(SH) \cdot NH \cdot C_6H_5$, was made by the action of benzaldehyde on 4-phenylthiosemicarbazide. It melted at 190° and agreed in its properties with those described by Pulvermacher (*loc. cit.*). It was boiled for half an hour with an alcoholic solution of ferric chloride. The product, which separated on dilution and evaporation of the alcohol, was treated with caustic soda. The resulting base, which melted at 199—200°, was easily soluble in boiling alcohol. It formed a hydrochloride insoluble in water but soluble in alcoholic hydrochloric acid. With acetic anhydride, it formed an acetyl derivative melting at 140°. The properties of the base agree fully with Marckwald and Bott's (*loc. cit.*) description of phenylaminophenylthiodiazole, $C_6H_5 \cdot C \begin{smallmatrix} N \cdot N \\ \diagup \quad \diagdown \\ S \end{smallmatrix} C \cdot NH \cdot C_6H_5$.

0.3464 gave 3.3266 $BaSO_4$. S = 12.35.

$C_{14}H_{11}N_3S$ requires S = 12.65 per cent.

When an alcoholic solution of the base is poured into alcoholic silver nitrate, a white precipitate is formed. On analysis:

0.6860 gave 0.2070 Ag. Ag = 30.17.

$C_{14}H_{10}N_3S$ Ag requires Ag = 30.00 per cent.

This silver derivative when air-dried is stable at the ordinary temperature; when suddenly heated, it decomposes with explosive violence and with the evolution of phenylisocyanitrile.

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