LVI.—*Halogen Additive Products of Substituted Thiosinnamines.*

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IN a paper communicated some years ago to this Society (Trans., 1892, **61**, 545), I showed that dibromopropylthiocarbimide,

when brought into contact with aniline, affords not dibromopropylthiocarbamide, but a saline compound of the formula

the results of further investigation are embodied in a paper recently published (this vol., p. 17), in which it is shown that the thiocarbimide in question acts on ammonia and on primary or secondary bases, affording in each case the hydrobromide of a corresponding penthiazoline, the interaction occurring probably in accordance with the general scheme

It has moreover been established in the latter communication that Maly's "thiosinnamine dibromide," $\text{C}_4\text{H}_8\text{N}_2\text{S}\cdot\text{Br}_2$ (*Zeit. f. Chem.*, 1867, 42), obtained from bromine and allylthiourea, is identical with the product of the action of ammonia on dibromopropylthiocarbimide, and is accordingly the hydrobromide of a brominated penthiazoline.

From the latter result, it appeared probable that the same substituted penthiazolines as are obtained from the thiocarbimide and organic

bases would be formed on treating the corresponding substituted allylthiocarbamides with bromine; and some experiments in the direction indicated were therefore undertaken.

Allylphenylthiocarbamide was first tried, the alcoholic solution being mixed with bromine (diluted with chloroform) in the proportions required by the equation

Interaction at once took place, but not in the way expected; the mixture quickly became turbid, and on warming to expel the solvents, yellow masses of sulphur were deposited, and an oily basic liquid remained, from which, however, no penthiazoline could be extracted.

Substituting allylorthotolylthiocarbamide, the result was somewhat better; no sulphur was produced, and on evaporation a sticky oil was left, out of which solid matter gradually separated, apparently the wished for tolyl derivative in an impure condition, which was but little improved by repeated recrystallisation. As this orthotolyl compound had already proved difficult to isolate (*loc. cit.*, 28), the product was set aside until an experiment could be made, using allylparatolylthiocarbamide, a substance likely, judging from previous work on the para-base, to afford a more satisfactory result.

At this stage, however, the question of bromine addition was definitely settled by the appearance in the last issue of the Society's Journal of an abstract of a paper by Gadamer (*Arch. Pharm.*, 1895, 233, 646—684), this chemist having directly obtained the brominated additive compounds of methylallyl-, dimethylallyl-, and (?) trimethylallyl-thiocarbamides respectively, by mixing their alcoholic solutions with bromine also dissolved in alcohol.

These substances appear to be regarded as merely additive compounds, but their recorded properties sufficiently resemble those of the penthiazoline derivatives above mentioned to leave practically no doubt that they are members of the latter class. "Methylallylthiocarbamide dibromide," for example, $\text{C}_8\text{H}_{10}\text{N}_2\text{SBr}_2$, forms, according to Gadamer, large white crystals, very soluble in water, and melting at $145\text{--}146^\circ$. On treatment with silver chloride, it yields a "chlorobromide," readily soluble in water, which melts at $120\text{--}123^\circ$; moreover, it affords a *picrate* and an *aurochloride* (melting at 182° and 80° respectively), and a yellow *platinochloride*.

To make certain, the compound was prepared by slowly adding bromine (1 mol.) in chloroform to methylallylthiocarbamide (1 mol.) dissolved in alcohol and cooled by a freezing mixture. Union took place with great energy, and, on concentration, the product was obtained as a white, crystalline solid, which, after recrystallisation from moderately strong alcohol, melted at $145\text{--}146^\circ$, gave with picric

acid the yellow, crystalline picrate, and otherwise answered to the description of Gadamer's compound. The yield of recrystallised material was about 76 per cent. of the theoretical.

Some of the pure substance was dissolved in water, and the strongly acid solution mixed with excess of dilute caustic potash. A clear, almost colourless oil was at once deposited, but soon hardened; it was removed, well washed with water, and dissolved in hot, slightly diluted alcohol, from which, however, it separated as an oil, which did not solidify even when kept many days in a desiccator or under diminished pressure. The oil was nearly insoluble in water, slightly alkaline to test paper, had, especially when warm, a faint, rather unpleasant, basic odour, and was freely soluble in alcohol or acids. It contained bromine and sulphur, though withholding the latter from both alkaline lead and ammoniacal silver salts even on boiling. On examining the alkaline solution from which the organic base had been precipitated,* it was found to contain, in addition to a little base (which gradually separated from it on standing) much potassium bromide.

The oil was analysed for sulphur, with the following results.

0.1932 gave 0.2145 BaSO₄. S = 15.26.

C₅H₉BrN₂S requires S = 15.33,

Consequently the aqueous "dibromide" under the influence of dilute alkali loses half its bromine as hydrogen bromide, leaving a basic residue, C₅H₉N₂SBr, the latter being presumably μ -methyl- γ -bromopentthiazoline, and the former its hydrobromide, which had been produced in the manner represented by the equation

The "chlorobromide" obtained from the "dibromide" by acting on it with silver chloride, was doubtless the hydrochloride of the brominated base, that is, C₅H₉N₂SBr.HCl. In order to obtain it, the base was treated with hydrochloric acid, in which it readily dissolved, and the solution concentrated on the water bath; the clear brown acid syrup which was left became tough on standing, but did not crystallise.

The methyl derivative, like several of the pentthiazolines already mentioned, gave, on treatment of the alcoholic solution with (neutral or ammoniacal) silver nitrate, an insoluble silver compound, very sensitive even to dim daylight; the yellowish-white precipitate retains its colour if kept in the dark, but rapidly changes on exposure to actinic light, through mauve and reddish, to deep purple.

* 11.5 grams of "dibromide" afforded 7 grams of brominated base, equal to 84.3 per cent. of the theoretical.

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It remained to examine the action of dibromopropylthiocarbimide on methylamine.

The above constituents, in molecular proportion, were dissolved separately in alcohol, and the solution mixed, when, after a few seconds, a very vigorous action commenced, a portion of the contents being projected out of the vessel; on concentrating the residue and allowing it to stand, solid matter separated; this, when purified by recrystallisation and washing with alcohol, had the appearance and exhibited all the properties of the compound obtained by Gadamer from bromine and methylallylthiocarbamide, save that its melting point was not quite sharp (144—146°).

Secondary bases, as I have shown (*loc. cit.*), for instance, methylaniline and piperidine, also unite with dibromopropylthiocarbimide, affording disubstituted penthiazolines

hence it may be safely concluded that Gadamer's dimethylallylthiocarbamide dibromide, and the chlorobromide which it gives with silver chloride, are the hydrobromide and hydrochloride respectively of the brominated base, μ -dimethyl- γ -brompenthiazoline,

Mention is made in the abstract above referred to of a *trimethylallylthiocarbamide* (from allylthiocarbimide and trimethylamine, at 150—160°) and its *dibromide*. If the former be really a thiocarbamide, its synthesis has a special interest, as being the only one of its kind hitherto effected. Allylthiocarbimide and triethylphosphine unite (Hofmann, *Ann.*, Suppl., 1, 47) to form a compound, $\text{C}_{10}\text{H}_{20}\text{NPS} = (?) (\text{C}_2\text{H}_5)_2\text{P}\cdot\text{CS}\cdot\text{N}(\text{C}_2\text{H}_5)(\text{C}_3\text{H}_5)$; but the only nitrogenous bases which have so far been combined with the thiocarbimides are those in which at least one typical hydrogen atom of the parent NH_3 is still retained.

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