

XXXIII.—*The Action of Isothiocyanates on the Aldehyde-ammonias.*

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Acetaldehyde-ammonia is known to combine with certain of the "mustard-oils;" thus, R. Schiff (*Ber.*, 9, 565) has described compounds obtained by the action of the former on ethyl-, allyl-, and phenyl-thiocarbimides respectively.

Some time ago, happening to have in my possession a quantity of benzylthiocarbimide, I tried its action on acetaldehyde-ammonia; with the result that the two substances readily combined under the following conditions:—

1 mol. of benzylthiocarbimide, dissolved in a small quantity of strong alcohol, was mixed with a concentrated alcoholic solution of 2 mols. of aldehyde-ammonia. The mixture was gently warmed on the water-bath, and in a few minutes solid matter began to separate; on removing the dish from the water-bath, the contents almost immediately set to a white crystalline mass. This was drained on the filter-pump, and pressed between filter-paper. It was then shaken up with cold spirit, and again drained and pressed. On carefully recrystallising the product from hot absolute alcohol, a woolly mass of white, shining needles was obtained, which was dried over sulphuric acid under the air-pump receiver.

The substance is sparingly soluble in cold alcohol; it dissolves tolerably freely in boiling alcohol, by which, however, it is gradually decomposed, with evolution of ammonia and aldehyde. It is insoluble in water, sparingly soluble in ether and bisulphide of carbon, more easily in chloroform. Benzene when hot dissolves it moderately, but when cold very sparingly. It melts at 175° with browning and copious evolution of gas. The alcoholic solution is slowly desulphurised by boiling with alkaline lead tartrate;\* with excess of silver nitrate a white precipitate separates, which on standing quickly blackens. Ammoniacal silver nitrate gives a yellow precipitate which blackens on boiling.

The substance was found to contain carbon, hydrogen, nitrogen, and sulphur.

On analysis, the following data were obtained:—

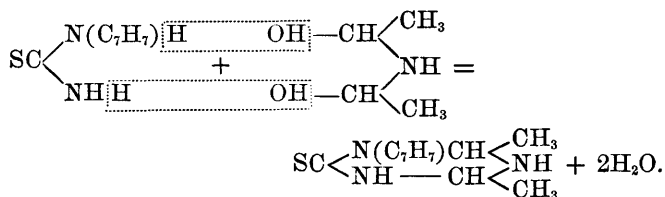
0·2192 gram burnt with lead chromate gave 0·1507 H<sub>2</sub>O and 0·4966 CO<sub>2</sub>,

or C = 61·78, H = 7·66.

\* Described by Emerson Reynolds, *Trans.*, 1884, 162.



We may suppose, now, that in the case of benzylthiocarbimide, the  $\text{NH}_3$ , which 2 mols. of aldehyde-ammonia can afford (as above), instead of being evolved, is fixed by the thiocarbimide, forming, perhaps, for the moment, benzylthiocarbamide, which then reacts with the aldehyde-ammonia residue—



Thus the compound of benzylthiocarbimide with aldehyde-ammonia would be a benzylated derivative of Nencki's "*Diäthyliden-thioharnstoffammoniak*."

The first question now was—can homologues of methyl be substituted for the *methyl*-groups? The answer was obtained as follows:—

1 mol. benzylthiocarbimide, dissolved in spirit, was added to a spirituous solution containing 2 mols. of ordinary (hydrated) isovaleraldehyde-ammonia. Crystals soon began to separate, and the mixture was exposed freely to the air (at ordinary temperature) till most of the liquid had evaporated. The crystalline mass was drained, and pressed on the filter-pump, washed lightly with spirit, and dissolved in hot absolute alcohol. The latter somewhat decomposed the substance,—valeraldehyde and ammonia being evolved,—but, on cooling, beautiful, snow-white, silky needles separated, forming a felted mass which retained much mother-liquor. It was thrown on the filter-pump, washed repeatedly with cold alcohol, and dried over sulphuric acid in a vacuum.

The substance is insoluble in water, soluble easily in hot, sparingly in cold alcohol, soluble in chloroform, ether, and bisulphide of carbon, and easily soluble in warm benzene. It melts at 161–162° with decomposition. Silver nitrate gives a finely granular, white precipitate, which blackens gradually on standing, or instantly on addition of ammonia. The alcoholic solution is slowly desulphurised by boiling with alkaline lead solution.

The following data were obtained on analysis:—

0.2313 gram, burnt with lead chromate, gave 0.5764  $\text{CO}_2$  and 0.1932  $\text{H}_2\text{O}$ ,

or C = 67.96 per cent. ; H = 9.28 per cent.

0.2264 gram gave 0.5639  $\text{CO}_2$  and 0.1875  $\text{H}_2\text{O}$ ,

or C = 67.92 per cent. ; H = 9.20 per cent.

0.2564 gram, burnt with copper oxide, gave 29 c.c. N at 9° C. and 755 mm.,

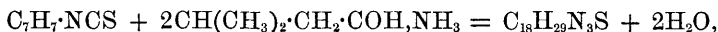
or 13.50 per cent. N.

0.3042 gram, evaporated to dryness with sodium hydrate in a nickel crucible and fused with potassium nitrate,\* gave 0.2170 BaSO<sub>4</sub>, or S = 9.80 per cent.,

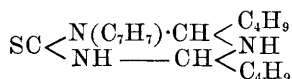
which agrees with the formula C<sub>18</sub>H<sub>29</sub>N<sub>3</sub>S.

		Theory.	Experiment.			
			I.	II.	III.	IV.
C <sub>18</sub>	215.46 .....	67.65	67.96	67.92	—	—
H <sub>29</sub>	29.00 .....	9.10	9.28	9.20	—	—
N <sub>3</sub>	42.03 .....	13.19	—	—	13.50	—
S	31.98 .....	10.04	—	—	—	9.80
318.47		—	—	—	—	—

The reaction may be represented thus:—



and the provisional formula ascribed is—



This compound is accordingly homologous with that previously described, butyl-groups being substituted for the methyl-groups.

The next question was: Can other radicles be substituted for the benzyl-group? To this an affirmative answer was also obtained.

(a.) *Ethylthiocarbimide and Aldehyde-ammonia.*†

Warm, concentrated alcoholic solutions of ethylthiocarbimide (1 mol.) and aldehyde-ammonia (2 mols.) were mixed. On cooling, crystals separated, which were collected and pressed. After two recrystallisations from spirit, they were found to melt—though not without decomposition—at 135—136°. At a few degrees higher they decompose completely, with evolution of gas.

\* This is the method now regularly used by Professor Reynolds for the determination of sulphur (and halogens) in suitable thio-compounds; it gives very satisfactory results. The details will probably be published shortly.

† By the action of aldehyde-ammonia on ethylthiocarbimide, R. Schiff obtained results which will be referred to later on.

Analytical data:—

0·2419 gram, burnt with lead chromate, gave 0·4315 CO<sub>2</sub> and 0·1911 H<sub>2</sub>O,

or C = 48·64; H = 8·77.

0·2534 gram, burnt with copper oxide, gave 54·1 c.c. N at 10° C and 742 mm.,

or N = 24·94 per cent.

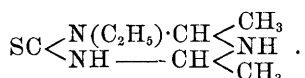
0·3394 gram, evaporated to dryness with sodium hydrate solution and fused with nitre, gave 0·4484 gram BaSO<sub>4</sub>,

or S = 18·16 per cent.

This agrees with the formula C<sub>7</sub>H<sub>15</sub>N<sub>3</sub>S.

		Theory.	Experiment.		
			I.	II.	III.
C <sub>7</sub>	83·79 .....	48·49	48·64	—	—
H <sub>15</sub>	15·00 .....	8·68	8·77	—	—
N <sub>3</sub>	42·03 .....	24·32	—	24·94	—
S	31·98 .....	18·50	—	—	18·16
172·80		—	—	—	—

The structural formula may be provisionally written—



*Allylthiocarbimide and Aldehyde-ammonia.\**

The allyl compound was prepared similarly to the preceding. It formed white woolly masses of needles, which after two recrystallisations from spirit, melted at 108—109°.

Analytical data:—

0·2057 gram, burnt with lead chromate, gave 0·3913 CO<sub>2</sub> and 0·1621 H<sub>2</sub>O,

or C = 51·87; H = 8·75.

0·2465 gram, burnt with copper oxide, gave 47·6 c.c. N at 12° C. and 767 mm.,

or N = 23·13 per cent.

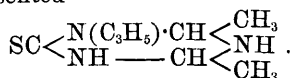
\* See note under ethylthiocarbimide; *ante*.

0.1423 gram, evaporated to dryness with sodium hydrate solution, and fused with nitre, gave 0.1820 BaSO<sub>4</sub>  
or S = 17.58 per cent.,

from which the formula C<sub>8</sub>H<sub>15</sub>N<sub>3</sub>S is deduced.

		Theory.	Experiment.		
			I.	II.	III.
C <sub>8</sub>	95.76 .....	51.83	51.87	—	—
H <sub>15</sub>	15.00 .....	8.11	8.75	—	—
N <sub>3</sub>	42.03 .....	22.75	—	23.13	—
S	31.98 .....	17.30	—	—	17.58

which may be represented—



(b.) *Phenylthiocarbimide and Aldehyde-ammonia.\**

Warm, concentrated alcoholic solutions of 1 mol. thiocarbimide and 2 mols. aldehyde ammonia were mixed. The mixture "set" instantly to a yellowish-white paste. This was freed from the mother-liquor, which it obstinately retains, by squeezing in a cloth. The mass was recrystallised three times from warm alcohol, and the product dried over sulphuric acid in a vacuum. The pure substance thus obtained crystallises in fine, silver-white needles, which melt at 148—149°, with browning and copious evolution of gas.

The substance is insoluble in water, but decomposed by boiling with it; soluble in alcohol, ether, and chloroform. The alcoholic solution is freely desulphurised by warming with alkaline lead solution. Silver nitrate in excess gives a white precipitate, which rapidly blackens, even in a freezing mixture.

Results of analysis:—

0.2020 gram, burnt with lead chromate, gave 0.4405 CO<sub>2</sub> and 0.1331 H<sub>2</sub>O,

or C = 59.46 per cent.; H = 7.32 per cent.

0.2188 gram gave 0.4769 CO<sub>2</sub> and 0.1465 H<sub>2</sub>O,

or C = 59.43 per cent.; H = 7.43 per cent.

0.2070 gram, burnt with copper oxide, gave 32.6 c.c. N, at 9° C. and 777 mm.,

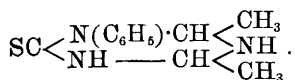
or N = 19.36 per cent.

\* See note under ethyl thiocarbimide, *ante*.

0.4600 gram evaporated to dryness with sodium hydrate solution and fused with nitre, gave 0.4943 gram  $\text{BaSO}_4$ ,  
 or S = 14.77 per cent.,  
 from which the formula  $\text{C}_{11}\text{H}_{15}\text{N}_3\text{S}$  is deduced.

		Theory.	Experiment.			
			I.	II.	III.	IV.
$\text{C}_{11}$	131.67.....	59.66	59.46	59.43	—	—
$\text{H}_{15}$	15.00.....	6.79	7.32	7.43	—	—
$\text{N}_3$	42.03.....	19.04	—	—	19.36	—
S	31.98.....	14.49	—	—	—	14.77

The structural formula (provisional) is—



A homologue of the latter was next obtained.

(c.) *Phenylthiocarbimide and Valeraldehyde-ammonia.*

Alcoholic solutions were mixed; on warming, a precipitate separated, which was drained and pressed. The mass was twice recrystallised from alcohol. Fine snowy-white needles were thus obtained, which, when dried over sulphuric acid in a vacuum, melt with decomposition at 152—153°. The dry substance becomes so electrical on slight friction that the particles fly about.

The following data were obtained :—

0.2057 gram, burnt with lead chromate, gave 0.5036  $\text{CO}_2$  and 0.1780  $\text{H}_2\text{O}$ ,  
 or C = 66.76 per cent.; H = 9.61 per cent.

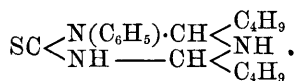
0.2043 gram, burnt with copper oxide, gave 23.4 c.c. N at 7° C. and 77 mm.,  
 or N = 14.07 per cent.

0.2988 gram treated with sodium hydrate and nitre (see above) gave 0.2330  $\text{BaSO}_4$ ,  
 or S = 10.72 per cent.,

which agrees with the formula  $\text{C}_{17}\text{H}_{27}\text{N}_3\text{S}$ .

		Theory.	Experiment.		
			I.	II.	III.
C <sub>17</sub>	203·49 .....	66·83	66·76	—	—
H <sub>27</sub>	27·00 .....	8·86	9·61	—	—
N <sub>3</sub>	42·03 .....	13·80	—	14·07	—
S	31·98 .....	10·50	—	—	10·72

The structural formula may be written—



(d.) *Orthotolylthiocarbimide and Aldehyde-ammonia.*

These substances unite at once when warm alcoholic solutions are mixed, the contents of the vessel "setting" to a snow-white mass. The yield is large—over 90 per cent. of the theoretical, but as this substance, like all the preceding, is decomposed by hot alcohol, the final yield of pure substance is small. The crude compound was recrystallised three times from warm alcohol: thus were obtained short, white prisms, insoluble in water, and melting at 158—159° with decomposition and evolution of gas.

The substance, dried over sulphuric acid in a vacuum, gave the following results on analysis:—

0·2264 gram, burnt with lead chromate, gave 0·5075 CO<sub>2</sub> and 0·1548 H<sub>2</sub>O,

or C = 61·13; H = 7·59.

0·2930 gram, burnt with copper oxide, gave 45·1 c.c. N, at 10° C. and 755 mm.,

or N = 18·30 per cent.

0·3250 gram, treated with sodium hydrate and nitre, gave 0·3236 BaSO<sub>4</sub>

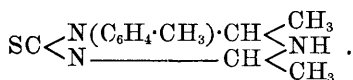
or S = 13·68 per cent.,

from which the formula C<sub>12</sub>H<sub>17</sub>N<sub>3</sub>S is deduced.

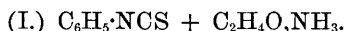


		Theory.	Experiment.		
			I.	II.	III.
C <sub>12</sub>	143·64 .....	61·21	61·13	—	—
H <sub>17</sub>	17·00 .....	7·24	7·59	—	—
N <sub>3</sub>	42·03 .....	17·91	—	18·30	—
S	31·98 .....	13·62	—	—	13·68

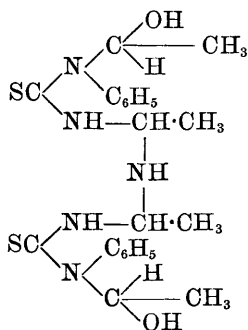
The reaction may be formulated as in the case of the isomeric benzyl compound, and the structure represented thus:—



Reference has been made in the early part of this paper to the fact that R. Schiff (*Ber.*, 9, 565) has also obtained compounds by the union of aldehyde-ammonia with certain "mustard oils." As his method of operating was essentially the same as that which I have described above, whilst on the other hand, the resulting compounds were quite different, I must indicate briefly the nature of his results.



By the action of these substances upon one another in alcoholic solution, Schiff obtained a compound to which he assigns the formula  $\text{C}_{22}\text{H}_{31}\text{N}_5\text{O}_2\text{S}_2$ . The structure he considers may be expressed by the following formula, which though not proved, "accords perfectly with the mode of formation and reactions."



The melting point of this substance is given at 148°; the compound which I obtained from the same materials melts at 148—149°.

For the purpose of comparison, I here tabulate the analytical results obtained by Schiff and by myself, together with the values calculated for the respective formulæ  $C_{22}H_{31}N_5O_2S_2$  and  $C_{11}H_{15}N_3S$ .

	$C_{22}H_{31}N_5O_2S_2$ (Schiff).				$C_{11}H_{15}N_3S$ (Dixon).		
	Theory.	Experiment.			Theory.	Experiment.	
		I.	II.			I.	II.
C .....	57·22	57·53	57·26	C .....	59·66	59·46	59·43
H .....	6·73	7·05	6·95	H .....	6·79	7·32	7·43
N .....	15·21	15·30	—	N .....	19·04	19·36	—
S .....	13·89	14·42	—	S .....	14·49	14·77	—
O .....	6·95	—	—				

(II.)  $C_3H_5 \cdot NCS + C_2H_4O, NH_3$ .

The compound obtained by the union of these compounds is described as having a similar constitution to the preceding. Empirical formula  $C_{16}H_{31}N_5S_2O_2$ ; m. p. 107—108°. The compound similarly obtained by myself has the empirical formula  $C_8H_{15}N_3S$ ; m. p. 108—109°.

I append, as before, a table of analytical results with corresponding calculated values.

	$C_{16}H_{31}N_5S_2O_2$ (Schiff).			$C_8H_{15}N_3S$ (Dixon).	
	Theory.	Experiment.		Theory.	Experiment.
C .....	49·30	49·30	C .....	51·82	51·87
H .....	7·98	8·12	H .....	8·11	8·75
N .....	18·03	—	N .....	22·75	23·13
S .....	16·46	—	S .....	17·30	17·58
O .....	8·23	—			

(III.)  $C_2H_5 \cdot NCS + C_2H_4O, NH_3$ .

The compound of ethylthiocarbimide with aldehyde-ammonia obtained similarly to the two preceding compounds, is described as having an analogous composition, and to it a similar structure is assigned. The melting point is given as 118—119°. Empirical formula  $C_{14}H_{31}N_5S_2O_2$ . The compound obtained by me corresponds

with the description "white silvery needles" given by Schiff to the ethyl-compound; but its melting point is, as already stated, 135—136°, and its empirical formula  $C_7H_{15}N_3S$ .

As before, I give a table of comparative data.

	$C_{14}H_{31}N_3S_2O_2$ (Schiff).			$C_7H_{15}N_3S$ (Dixon).	
	Theory.	Experiment.		Theory.	Experiment.
C .....	45·97	46·30	C .....	48·49	48·64
H .....	8·50	8·50	H .....	8·68	8·77
N .....	19·21	—	N .....	24·32	24·94
S .....	17·54	—	S .....	18·50	18·16
O .....	8·78	—			

As I have directly determined all the constituents of each of the substances I obtained, and the analyses add up fairly satisfactorily, it is obviously impossible to admit that my compounds contain oxygen; yet their characters agree, in the main, with those described by Schiff. In his paper he states, that experiments directed with a view to determine whether hydroxyl-groups (whose existence he assumes) were present, led to no result. If the substances I obtained are really identical with Schiff's compounds, I can only conclude that he did not obtain them in a sufficiently pure state for analysis.

The structural formulæ given by myself are only provisional, but I hope shortly to be in a position to make a further communication, in which the constitution of these compounds shall be dealt with.

*Chemical Laboratory,*  
*University of Dublin,*  
*March 1st, 1888.*