

ON CARBOLTHIONIC ACIDS AND THEIR ESTERS. PART IV.
A NEW METHOD OF FORMATION FOR THIAMIDES
AND THIOHYDRAZIDES.

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Thiamides have hitherto been prepared either by the interaction between amides and phosphorus pentasulphide or by the addition-reaction of nitriles toward hydrogen sulphide. But both methods are not widely applicable, and as the consequence thiamides hitherto known have been very limited in number.

Now the reactions⁽¹⁾ between carbolthionic esters (thiocarboxylic o-esters) and ammonia or amines, which take place in the ethereal solution so as to yield thiamides, were experimentally confirmed to afford a very widely applicable new method for formation of various thiamides.

(1) *Mem. Coll. Sci. Eng., Kyoto*, 3 (1912), 248.

Phenylhydrazine also reacts upon carbolthionic esters in the ethereal solution just analogously and yields various thiohydrazides many of which are quite new substances hitherto unknown.

Those thiamides and thiohydrazides prepared according to this method are described below.

I. Thiamides.

1. *Thioacetoethylamide*, $\text{CH}_3\text{CSNHC}_2\text{H}_5$. When an ethereal solution of methylcarbolthionic propylester (thioacetic o-propylester) added with some ethylamine was left to stand for a few days it gradually lost its characteristic odour and colour, and a thick yellow oil having a peculiar odour separated out on the bottom of the flask. The oil was purified by washing it repeatedly with ether, and analysed.

0.1324 Gr. the substance gave 0.3136 gr. Ag_2S ; $\text{S}=30.64\%$ (Calc. 31.08).

Thioacetoethylamide is a yellow viscous liquid with a characteristic odour, soluble in alcohol and nearly insoluble in water and ether. When warmed with alkali it decomposes evolving ethylamine.

2. *Thiopropioethylamide*, $\text{C}_2\text{H}_5\text{CSNHC}_2\text{H}_5$. This was obtained from ethylcarbolthionic propylester and ethylamine as a yellow viscous liquid resembling the corresponding thioacetamide in every respect.

0.0996 Gr. the substance gave 0.2131 gr. Ag_2S ; $\text{S}=27.68\%$ (Calc. 27.36).

3. *Thiobenzo-ethylamide*, $\text{C}_6\text{H}_5\text{CSNHC}_2\text{H}_5$. This was prepared from phenylcarbolthionic butylester and ethylamine. It is also a yellow viscous liquid.

4. *Thiophenylaceto-ethylamide*, $\text{C}_6\text{H}_5\text{CH}_2\text{CSNHC}_2\text{H}_5$. This thiamide was also obtained as a yellow viscous liquid by the action of ethylamine upon benzylcarbolthionic isoamylester.

0.2184 Gr. the substance gave 0.2948 gr. Ag_2S ; $\text{S}=17.46\%$ (Calc. 17.89).

5. *Thioparatolu-ethylamide*, $\text{C}_7\text{H}_7\text{CSNHC}_2\text{H}_5$. Paratolylcarbolthionic propylester and ethylamine were used for the preparation of the thiamide which was also found to be a yellow thick oil.

0.0159 Gr. the substance gave 0.0212 gr. Ag_2S ; $\text{S}=17.25\%$ (Calc. 17.89).

6. *Thioaceto-isobutylamide*, $\text{CH}_3\text{CSNHC}_4\text{H}_9$. When prepared from methylcarbolthionic isoamylester and isobutylamine it was obtained as a yellow coloured oily substance.

0.1235 Gr. the substance gave 0.2293 gr. Ag_2S ; $\text{S}=24.02\%$ (Calc. 24.44).

7. *Thiopropio-isobutylamide*, $\text{C}_2\text{H}_5\text{CSNHC}_4\text{H}_9$. For the preparation ethylcarbolthionic butylester and isobutylamine were used, and it was obtained as a yellow thick oil.

- 0.1048 Gr. the substance gave 0.1796 gr. Ag_2S ; $\text{S}=22.17\%$ (Calc. 22.08).
8. *Thiobenzo-isobutylamide*, $\text{C}_6\text{H}_5\text{CSNHC}_4\text{H}_9$. This was obtained as a yellow crystalline substance when phenylcarbolthionic methylester was treated with isobutylamine. It was purified by recrystallizing from a mixture of alcohol and ether, in the former of which it is very soluble while in the latter hardly soluble.
- 0.1417 Gr. the crystal gave 0.1783 gr. Ag_2S ; $\text{S}=16.28\%$ (Calc. 16.60).
9. *Thiophenylaceto-isobutylamide*, $\text{C}_6\text{H}_5\text{CH}_2\text{CSNHC}_4\text{H}_9$. This was prepared from benzylcarbolthionic isobutylester and isobutylamine. A very viscous yellow liquid.
- 0.1702 Gr. the substance gave 0.2041 gr. Ag_2S ; $\text{S}=15.51\%$ (Calc. 15.47).
10. *Thioparatolu-isobutylamide*, $\text{C}_7\text{H}_7\text{CSNHC}_4\text{H}_9$. Paratolylcarbolthionic butylester and isobutylamine were used for the preparation. Yellow crystals with a peculiar odour.
- 0.0434 Gr. the crystal gave 0.0512 gr. Ag_2S ; $\text{S}=15.26\%$ (Calc. 15.47).
11. *Thioaceto-isoamylamide*, $\text{CH}_3\text{CSNHC}_5\text{H}_{11}$. This was prepared from methylcarbolthionic isobutylester and isoamylamine. A yellow thick liquid having a peculiar smell.
- 0.0702 Gr. the substance gave 0.1193 gr. Ag_2S ; $\text{S}=21.99\%$ (Calc. 22.08).
12. *Thiopropio-isoamylamide*, $\text{C}_2\text{H}_5\text{CSNHC}_5\text{H}_{11}$. Ethylcarbolthionic isoamylester and isoamylamine were used for this preparation and the amide was obtained as a yellow liquid.
- 0.0847 Gr. the substance gave 0.1306 gr. Ag_2S ; $\text{S}=19.95\%$ (Calc. 20.14).
13. *Thiobenzo-isoamylamide*, $\text{C}_6\text{H}_5\text{CSNHC}_5\text{H}_{11}$. For the preparation phenylcarbolthionic isoamylester and isoamylamine were used. It is a yellow crystalline substance.
- 0.1037 Gr. the crystal gave 0.1252 gr. Ag_2S ; $\text{S}=15.62\%$ (Calc. 15.47).
14. *Thiophenylaceto-isoamylamide*, $\text{C}_6\text{H}_5\text{CH}_2\text{CSNHC}_5\text{H}_{11}$. This was obtained from benzylcarbolthionic ethylester and isoamylamine as a yellow viscous liquid.
- 0.1894 Gr. the substance gave 0.2144 gr. Ag_2S ; $\text{S}=14.64\%$ (Calc. 14.49).
15. *Thioparatolu-isoamylamide*, $\text{C}_7\text{H}_7\text{CSNHC}_5\text{H}_{11}$. The thiamide was produced as a yellow crystalline substance when paratolylcarbolthionic methylester was treated with isoamylamine in an ethereal solution.
- 0.1042 Gr. the crystal gave 0.1143 gr. Ag_2S ; $\text{S}=14.19\%$ (Calc. 14.49).

II. Thiohydrazides.

Many thiohydrazides described below were prepared from carbolthionic esters by treating the latter with phenylhydrazine. They are all crystalline

solids of light yellow colour easily decomposed by alkali and acid.

1. *Thioacetophenylhydrazide*, $\text{CH}_3\text{CSNHNHC}_6\text{H}_5$.
0.0538 Gr. the substance gave 0.0801 gr. Ag_2S ; S=19.26% (Calc. 19.29).
2. *Thiopropiophenylhydrazide*, $\text{C}_2\text{H}_5\text{CSNHNHC}_6\text{H}_5$.
0.1323 Gr. the substance gave 0.1837 gr. Ag_2S ; S=17.96% (Calc. 17.79).
3. *Thiobenzophenylhydrazide*, $\text{C}_6\text{H}_5\text{CSNHNHC}_6\text{H}_5$.
0.0148 Gr. the substance gave 0.0159 gr. Ag_2S ; S=13.90% (Calc. 14.05).
4. *Thiophenylacetophenylhydrazide*, $\text{C}_6\text{H}_5\text{CH}_2\text{CSNHNHC}_6\text{H}_5$.
Not analysed.
5. *Thioparatoluphenylhydrazide*, $\text{C}_7\text{H}_7\text{CSNHNHC}_6\text{H}_5$.
0.0242 Gr. the substance gave 0.0249 gr. Ag_2S ; S=13.31% (Calc. 13.23).

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