LVII.—*Acidic Thiocarbimides, Thioureas, and Ureas.*

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IN communications recently made to this Society (Dixon and Doran, Trans., 1895, 565; Dixon, *ibid.*, 1040), evidence has been adduced to show that the interaction between lead thiocyanate and the acid chlorides of the forms $R'\cdot\text{CO}\cdot\text{Cl}$ and $R''(\text{CO}\cdot\text{Cl})_2$ constitutes a general method for the production of thiocarbimides of the acidic class. Thus, by heating valeryl and cinnamoyl chlorides, in dry benzene, with lead thiocyanate, the compounds $\text{C}_4\text{H}_9\cdot\text{CO}\cdot\text{NCS}$ and

were obtained in solution; and similarly from succinyl and phthalyl chlorides, the dithiocarbimides, $\text{C}_2\text{H}_4(\text{CO}\cdot\text{NCS})_2$ and $\text{C}_6\text{H}_4(\text{CO}\cdot\text{NCS})_2$, respectively.

Excepting that they are all more or less readily decomposed in presence of water

and cannot, consequently, be purified by steam distillation, the acidic thiocarbimides, so far obtained, resemble, in general, their congeners of the non-acidic class. They are extremely reactive, have a pungent and rather characteristic odour, and combine readily with alcohols, with phenylhydrazine, with ammonia,† and with (primary or secondary) amines, yielding the corresponding thiocarbamates, semithiocarbazides, and thioureas.

In connection with the last-named class of interaction, it may be noted that, whereas between non-acidic thiocarbimide and primary amine, the radicles may be exchanged without affecting the result—thus, for instance, *ab*-ethylphenylthiocarbamide occurs indifferently from the union of either ethylthiocarbimide with phenylamine, or of phenylthiocarbimide with ethylamine—on the other hand, in the case of acidic thiocarbimides, the radicles are not thus interchangeable. Acetylthiocarbimide readily unites (Miquel, *loc. cit.*, 318) with phenylamine, affording *ab*-acetylphenylthiocarbamide—

but the converse process—

so far at least as my experiments have gone, cannot be directly realised.

* Sometimes carbonyl sulphide is formed; for instance, $\text{PhCO}\cdot\text{NCS} + \text{H}_2\text{O} = \text{PhCO}\cdot\text{NH}_2 + \text{COS}$ (Miquel, *Ann. Chim. Phys.* [5], 11, 300).

† Not always, however, so as to afford a thiourea as the end-product.

The work referred to in the papers above mentioned, and in other previous communications, originated in an examination of Miquel's "acetyl thiocyanate" (*loc. cit.*); this substance, however, in relation to bases, behaves generally as a thiocarbimide, and unless it, and its allies, be tautomeric, the true acidylthiocyanates apparently yet remain to be discovered. In the present communication, an account is given of an extension of the method in question to the preparation of certain thiocarbimides derived from acids which belong, either by structure or function, to the aliphatic class.

I. PROPIONYLTHIOCARBIMIDE, $C_2H_5 \cdot CO \cdot NCS$, AND ITS DERIVATIVES.

Propionyl chloride, when added to excess of dry, very finely divided lead thiocyanate, acted vigorously, without the application of heat, and by distilling off on the oil bath heated to about 180° , a clear, highly refracting liquid came over of pungent and tear-exciting odour, colourless at first, but becoming brownish on keeping. This liquid was miscible in all proportions with alcohol and ether but insoluble in cold water, slowly decomposing in contact with it, or more rapidly on heating, with formation of thiocyanic acid. Its alcoholic solution, when mixed with ammoniacal silver nitrate or alkaline lead tartrate, was copiously desulphurised on warming, thus indicating the presence of a thiocarbimide. Analysis was considered unnecessary, in view of the well-marked derivatives which it afforded when treated in solution with nitrogenous bases. The yield by the above method was very unsatisfactory, but by operating as described in former papers, namely, heating the constituents together in anhydrous benzene until the solution was free from chlorine, filtering, and further diluting the filtrate to a known strength (1 gram-molecule per litre, assuming quantitative interaction), a clear, pale yellowish, pungently smelling liquid was obtained, which subsequent experiment showed to contain at least 90 per cent. of the theoretical amount of propionylthiocarbimide.

This solution, when shaken up with cold water, gave a faint thiocyanic reaction, but, if boiled for a few seconds with it, afforded an intense blood-red coloration on the addition of ferric chloride. In the experiments next described, the benzene solution, prepared as above,* was employed.

ab-Propionylphenylthiocarbimide, $C_2H_5 \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5$.

Heat was evolved on mixing the thiocarbimide with aniline, both in benzene solution, and on concentration at the ordinary temperature,

* In one preparation, mercuric thiocyanate was used; it did not appear to possess any advantage over the lead salt.

and vitreous crystals separated; after being drained by aid of the pump, washed with spirit, and air-dried, the yield amounted to only about 66 per cent. of that obtainable according to the equation

and reckoned on the amount of chloride used. By repeated recrystallisation from boiling spirit, brilliant, long, colourless prisms were obtained, melting constantly at $129\text{--}130^\circ$ (corr.), without decomposition.

A sulphur determination served to establish the identity of the compound.

0.2018 gave 0.2295 BaSO_4 . $\text{S} = 15.63$.

$\text{C}_{10}\text{H}_{12}\text{N}_2\text{SO}$ requires $\text{S} = 15.40$ per cent.

Propionylphenylthiocarbamide is very sparingly soluble in boiling water, crystallising from it in slender needles, almost insoluble in the cold; moderately soluble in hot alcohol, ether, and carbon bisulphide, easily in hot benzene, very freely in chloroform. It also dissolves readily in dilute caustic alkali; the latter solution, when mixed with alkaline lead tartrate, is desulphurised freely by warming. Silver nitrate, if added to a cold, dilute alcoholic solution, affords a yellowish precipitate, rapidly changing, through orange and brown, to black; with the ammoniacal nitrate, silver sulphide is instantly formed.

Action of Caustic Alkali.—Cold, dilute caustic potash dissolves the thiocarbamide with decomposition; if dilute hydrochloric acid be now added to the clear solution, a white solid at once separates, which, after recrystallisation from dilute alcohol, forms white prisms, sparingly soluble in cold, moderately in hot, water, having an intensely bitter taste, melting at $153\text{--}154^\circ$, and consisting of *phenylthiourea*.

This decomposition (under the influence of cold, dilute caustic alkali) of symmetrical disubstituted thiocarbamides containing an acid radicle, into a salt of that acid and the corresponding monosubstituted thiourea, appears to be generic.

Action of Silver Nitrate.—By desulphurising a moderately concentrated, hot alcoholic solution of the thiocarbamide with a trifle over the calculated quantity of silver nitrate, filtering off the silver sulphide, and allowing the filtrate to evaporate slowly, a brownish solid was obtained, which, after several recrystallisations from spirit, yielded almost colourless, pearly flattened needles, melting, without decomposition, at $138\text{--}139^\circ$ (corr.), and consisting, as shown by the result of a nitrogen determination, of the expected *propionylphenylurea*, $\text{C}_2\text{H}_5\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$.

0.201 gave 25.6 c.c. moist nitrogen at 18° and 763.5 mm. $N = 14.78$.

$C_{10}H_{12}N_2O_2$ requires $N = 14.62$ per cent.

The same compound was obtained by Kühn (*Ber.*, **17**, 2881) from phenylic isocyanate and propionamide; m. p. 137°.

ab-Propionylorthotolylthiocarbamide, $C_2H_5 \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_4 \cdot CH_3$.

Molecular proportions of orthotoluidine and thiocarbimide were mixed in benzene; heat was evolved, and crystals quickly separated, which, after recrystallisation from alcohol, formed long, hair-like needles, melting between 143° and 144° (corr.). A sulphur determination afforded the following result.

0.2062 gave 0.2196 $BaSO_4$. $S = 14.64$.

$C_{11}H_{14}N_2SO$ requires $S = 14.43$ per cent.

The substance is insoluble in water, moderately soluble in hot alcohol, rather sparingly in cold, easily in warm, dilute caustic alkali; the latter solution, on the addition of hydrochloric acid, yields a white precipitate, amorphous at first, but soon becoming crystalline; when recrystallised from dilute alcohol, this forms colourless prisms, melting at 160—161° (corr.), and consisting of *orthotolylthiourea* [m. p. of CSN_2H_3O To, 160—161° (Trans., 1892, 525)]. With alkaline lead tartrate and neutral or ammoniacal silver salts, the propionyl compound behaves like the corresponding phenyl derivative.

ab-Propionylmetatolylthiocarbamide, $C_2H_5 \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_4 \cdot CH_3$.

This is prepared from the thiocarbimide and metatoluidine; the very sticky, semi-solid product, after being drained on porous clay, was twice recrystallised from boiling alcohol, and thus obtained in beautiful, long, vitreous prisms, melting at 86—87° (uncorr.).

A portion was analysed for sulphur.

0.2012 gave 0.2125 $BaSO_4$. $S = 14.52$.

$C_{11}H_{14}N_2SO$ requires $S = 14.43$ per cent.

The metatolyl compound is practically insoluble in water, but dissolves easily in dilute alkali; the solution, when mixed with a lead salt and heated, affording a speculum of galena. It is very freely soluble in hot alcohol, moderately in cold, and is desulphurised easily by neutral or ammoniacal silver nitrate.

ab-Propionylparatolylthiocarbamide, $C_2H_5 \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_4 \cdot CH_3$.

Prepared like its congeners, using paratoluidine; some reddish-yellow, oily bye-product was extracted by the aid of the pump, and the residue recrystallised from boiling spirit. Thus purified, the

compound formed long white needles, almost insoluble in water, moderately soluble in hot alcohol, much less so in cold, and melting at $127\cdot5$ — $128\cdot5^\circ$ (corr.), without decomposition.

Analysis gave the following result.

0.2 gave $0\cdot2114$ BaSO₄. S = 14.53.

C₁₁H₁₄N₂SO requires S = 14.43 per cent.

It dissolves freely in dilute caustic potash, and the solution is desulphurised readily, with formation of a speculum, on warming it with alkaline lead tartrate; the alcoholic solution, with neutral silver nitrate, affords at once, even in the cold, a precipitate of silver sulphide.

*n-Propionyl-ν-methylphenylthiourea,**

Methylaniline and the thiocarbimide spontaneously interacted with evolution of heat, and the solution, as it became concentrated, slowly deposited large, ice-like, crystalline masses. The product was broken up, a small quantity of brownish oil removed by the pump, the residue washed with light petroleum, dissolved in alcohol, in which it appears to be indefinitely soluble, concentrated, and set aside. Large vitreous prisms gradually separated, softening at 67° and melting at 68 — 69° (uncorr.).

Analysis.

0.2008 gave $0\cdot2104$ BaSO₄. S = 14.40.

C₁₁H₁₄N₂SO requires S = 14.43 per cent.

It is slightly soluble in hot water; the solution gives with silver nitrate a white precipitate soluble in ammonia; the latter solution does not blacken on boiling. It is freely soluble in cold alcohol and benzene, very freely in chloroform, and rather sparingly in hot light petroleum, from which, on cooling, it separates as an oil. The alcoholic solution is neutral; if silver nitrate be added to it no precipitate falls, but the mixture becomes sharply acid. The sulphur is not removed by boiling with alkaline lead tartrate.

n-Propionyl-ν-phenylbenzylthiourea,

Heat was evolved on mixing the constituents dissolved in benzene, and, as the latter evaporated, long prisms were slowly deposited, the yield amounting to almost 90 per cent. of the theoretical. The product was dissolved in boiling spirit, and, on cooling, thick, vitreous

* For nomenclature, see Trans., 1895, 67, 564.

prisms crystallised out, having a faint yellow tinge, and melting at 101—102° (corr.).

On analysis, the following figures were obtained.

0.2012 gave 0.158 BaSO₄. S = 10.79.

C₁₇H₁₈N₂SO requires S = 10.75 per cent.

Propionylphenylbenzylthiourea melts when heated with water, in which, however, it is practically insoluble; it is freely soluble in boiling alcohol, much more sparingly in cold. It dissolves also in caustic potash, but this solution, when mixed with alkaline lead tartrate, is not desulphurised by boiling. The sulphur is very tenaciously held; an alcoholic solution of the substance yields, with ammoniacal silver nitrate, a white precipitate, which dissolves on heating; if now the temperature be further raised, a white precipitate again forms, which does not blacken, even at the boiling point.

Propionylthiocarbimide and *piperidine* interacted with evolution of much heat and formation of thin pearly plates, free from odour, and melting at 92—93°. The solid product was very easily soluble in water and alcohol, sparingly in cold benzene; its solution was not desulphurised either by silver or by lead salts; with ferric chloride, it gave an intense reaction for thiocyanic acid, and when warmed with potash evolved an alkaline vapour smelling of piperidine. These properties are, in the main, inconsistent with those to be expected of propionylpiperidylthiourea, but indicate the presence of *piperidine thiocyanate*, C₅H₁₀NH₂HSCN. The latter view was confirmed by the result of a sulphur determination.

0.2038 gave 0.3323 BaSO₄. S = 22.41.

C₅H₁₀NH₂HSCN requires S = 22.23 per cent.

The action probably occurs as follows.

EtCO·NCS + C₅H₁₀·NH₂ + H₂O = C₅H₁₀·NH₂HSCN + EtCOOH, the crystalline product being identical in all respects with Gebhardt's (*Ber.*, 1884, **17**, 3041) "piperidylthiourea," a compound which Hofmann and Gabriel showed later (*ibid.*, 1892, **25**, 1588) to be, not a thiourea, but the isomeric thiocyanate.

α-Propionyl-β-phenylthiosemicarbazide,

C₂H₅·CO·NH·CS·NH·NH·C₆H₅ [or C₂H₅·CO·NH·C(SH):N·NH·C₆H₅].

Much heat was evolved on mixing the thiocarbimide with phenylhydrazine, and the mixture became turbid from separation of oily droplets; after allowing the benzene to evaporate spontaneously, a brownish oil was left, which in about a fortnight had changed to a yellow, semi-solid mass. The latter was dissolved in warm benzene,

precipitated by adding light petroleum, the precipitate freed by means of the filter-pump from some oily matter, washed, and dissolved in boiling alcohol. On cooling, tufts of very brilliant, white prisms were deposited; they shrank a little at about 150°, and melted at 155–156° (corr.), without decomposition.

Analytical data.

0.2007 gave 0.2127 BaSO₄. S = 14.57.

C₁₀H₁₃N₃SO requires S = 14.36 per cent.

The product is slightly soluble in water, moderately in boiling alcohol, rather sparing in cold, practically insoluble in light petroleum. Its solution gives, with ferric chloride, no colour change, but a finely divided whitish precipitate forms, resembling sulphur in appearance; copper sulphate produces a pale blue, amorphous precipitate. It is not desulphurised by alkaline lead tartrate; neither is the yellowish precipitate, which it yields with ammoniacal nitrate of silver, blackened on boiling for a short time. It is not decomposed by boiling with hydrochloric acid; it dissolves in (concentrated) sulphuric acid, and is vigorously attacked, with formation of a deep, orange-red liquid, on the addition of nitric acid.

Considerable additions have been made in recent years to our knowledge of the thiosemicarbazides; assuming them to be constituted on the type $\text{CS} \begin{smallmatrix} \text{NH}_2 \\ \text{NH} \cdot \text{NH}_2 \end{smallmatrix}$, we are now acquainted with such derivatives as, *e.g.*, (1) NPh·CS·NH·NH₂, (2) NH₂·CS·NPh, (3) NPh·CS·NH·NPh, (4) NH₂·CS·NH·NPh₂,

(5) NPh·CS·NPh·NPh, (6) NEtPh·CS·NH·NMePh.

To facilitate the nomenclature of this class of substances, and of the corresponding thiocarbazides (together with the oxygen analogues of both), I venture to suggest the following convention: the two nitrogen attachments in the urea or thiocarbamide nucleus being, as usual, designated *a* and *b* respectively, the further nitrogen attachments may be similarly indicated by *α* and *β*, thus

In this way the compounds above formulated would be distinguished as (1) *a*-phenyl-, (2) *β*-phenyl-, (3) *αβ*-diphenyl-, (4) *β*-diphenyl-, (5) *αββ*-triphenyl-, and (6) *a*-ethylphenyl-*β*-methylphenyl-thiosemicarbazides. If certain of the sulphuretted compounds are to be regarded as derivatives of the type NH₂·C(SH)·N·NH₂, the system of nomenclature proposed by me for thioureas (*Note*, p. 859) is equally applicable; in this case the *n*-attachment is no longer available for

substituting groups, and hence does not require to be specified; attachment at the end nitrogen atom (which latter is itself engaged at the *n*-position) may conveniently be defined by *N*, as shown in the diagram.

Thus, for instance, *p*ToNH·C(SH):N·NHPh and its isomer, NHPh·C(SH):N·NH*p*To, would be named *ν*-paratolyl-*N*-phenyl- and *ν*-phenyl-*N*-paratolyl-thiosemicarbazides respectively, the prefixes *syn*- and *anti*- serving further, if required, to distinguish the two stereoisomeric modifications of each of these compounds (Markwald, *Ber.*, 1892, **25**, 3098; Dixon, *Trans.*, 1892, **61**, 1012).

In addition to the experiments described above, propionylthiocarbimide, in benzene solution, was brought into contact with alcoholic ammonia, aldehyde-ammonia, and benzylic alcohol; in all cases interaction spontaneously occurred with evolution of heat, but the products were more or less unsatisfactory, and were not examined in detail.

II. ISOBUTYRYLTHIOCARBIMIDE, (CH₃)₂CH·CO·NCS, AND ITS DERIVATIVES.

Mercuric and lead thiocyanates were both employed in preparing the benzene solution of the above thiocarbimide; the lead salt is preferable to the mercuric, on account of the prolonged boiling necessary for complete decomposition when the latter is used. The product was a clear, pale yellow liquid, smelling faintly of butyric acid, having the characteristic thiocarbimide odour, and attacking the eyes, but to a much less extent than is the case with its lower homologues.

When shaken up with water and treated with ferric chloride, little change is produced; if, however, the mixture be heated to boiling, the deep blood-red thiocyanic coloration at once appears. On the other hand, the solution, when warmed with alkaline lead, or ammoniacal silver salts, affords a copious precipitate of metallic sulphide.

ab-Isobutyrylphenylthiocarbamide, C₃H₇·CO·NH·CS·NH·C₆H₅.

Obtained, with considerable evolution of heat, by mixing the thiocarbimide with alcoholic solution of aniline. On recrystallisation from spirit, the compound was deposited in large, colourless, vitreous prisms, free from odour, and melting at 128·5–129·5° (corr.), without

decomposition. The yield was only 50 per cent. of the theoretical. A sulphur determination was made with the following result.

0.2019 gave 0.2172 BaSO₄. S = 14.77.

C₁₁H₁₄N₂SO requires S = 14.43 per cent.

Isobutyrylphenylthiocarbamide is insoluble in water, easily soluble in boiling alcohol, moderately in cold, freely in chloroform, ether, and hot benzene, rather sparingly in boiling, light petroleum, from which, on cooling, it separates in short, extremely brilliant, seemingly rhombic prisms. It dissolves easily in warm, dilute, caustic potash; this solution, with hydrochloric acid, gives a white precipitate consisting of phenylthiourea, and is desulphurised by heating with alkaline lead tartrate. The cold alcoholic solution is rapidly desulphurised by either neutral or ammoniacal silver nitrate.

Action of Silver Nitrate.—By desulphurising the hot alcoholic solution with this reagent, the corresponding *ab-isobutyrylphenylurea* was obtained; after several recrystallisations from spirit it formed slender needles melting at 139—140° (141—142° corr.).

Analysis

0.1992 gave 23.5 c.c. N at 16° and 756 mm. N = 13.67.

C₁₁H₁₄N₂O₂ requires N = 13.62.

The urea is insoluble in water, very freely soluble in hot alcohol, and easily so in the cold; the same compound was obtained by Pinner (*Imidoäther*, 124) by boiling butenyldiphenyldiureide with acetic acid; m. p. 140°.

ab-Isobutyrylorthotolylthiocarbamide, C₃H₇CO·NH·CS·NH·C₆H₄·CH₃.

Prepared as before, using orthotoluidine; crystals were deposited on cooling, the yield of which, after draining and washing with spirit, amounted to about 90 per cent. of the theoretical. When recrystallised from alcohol, the substance formed short, pure white needles melting, without decomposition, at 136—137° (corr.).

The following result was obtained on analysis.

0.203 gave 0.1976 BaSO₄. S = 13.38.

C₁₂H₁₆N₂SO requires S = 13.57 per cent.

The compound is insoluble in water, easily soluble in hot alcohol, rather sparingly in cold, freely in ether and benzene, very freely in chloroform. Its solution in dilute caustic alkali gives a white precipitate on the addition of hydrochloric acid; if mixed with alkaline lead tartrate and heated, a brilliant galena mirror is formed. With neutral and ammoniacal silver salts it behaves like the preceding thio-compound.

ab-Isobutyrylorthotolylurea was produced by acting on the hot

alcoholic solution with the calculated amount of silver nitrate; after several recrystallisations from alcohol, in which it is very freely soluble at the boiling point, it was obtained in long, satiny, flexible needles insoluble in water, moderately soluble in cold alcohol or hot light petroleum, easily in ether and benzene, very freely in chloroform. Its melting point was $134-135^{\circ}$ (corr.).

A nitrogen determination afforded the following result.

0.2054 gave 23 c.c. moist nitrogen at 16° and 757 mm. $N = 12.99$.

$C_{12}H_{16}N_2O_2$ requires $N = 12.76$ per cent.

ab-Isobutyrylparatolylthiocarbamide, $C_3H_7 \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_4 \cdot CH_3$.

Obtained like the corresponding ortho-derivative; on concentration, very large, ice-like prisms were formed, melting, after recrystallisation, at $134-135^{\circ}$ (corr.), undecomposed. The yield was about 75 per cent. of the theoretical.

Analysis.

0.2002 gave 0.2033 $BaSO_4$. $S = 13.96$.

$C_{12}H_{16}N_2SO$ requires $S = 13.57$ per cent.

The paratolyl derivative is insoluble in water, easily soluble in hot alcohol, moderately in cold, crystallising therefrom in brilliant prisms; it is very freely soluble in chloroform, freely in benzene, moderately in boiling light petroleum. It dissolves readily in warm dilute caustic potash; this solution is desulphurised by heating with alkaline lead tartrate, yielding a brilliant speculum, and is precipitated by hydrochloric acid. With ammoniacal or neutral silver nitrate, it is desulphurised in the cold, but not quite so readily as the orthotolyl analogue.

ab-Isobutyrylparatolylurea was easily obtained by treatment with the last-named salt; after three recrystallisations from spirit, the product still retained a faint salmon-pink colour, which was removed by treatment with animal charcoal. In this way pure white, silky needles were obtained, becoming electrical on friction and melting at $138-139^{\circ}$ (corr.).

Analysis.

0.2006 gave 22.1 c.c. at 13° and 755 mm. $N = 12.93$.

$C_{12}H_{16}N_2O_2$ requires $N = 12.76$ per cent.

The substance is insoluble in water, and, like the phenyl and orthotolyl analogues, is conveniently obtained by precipitating the dark coloured filtrate from the silver sulphide with excess of water. It is very freely soluble in hot alcohol, easily in cold, moderately in cold benzene.

ab-Isobutyrylalphanaphthylthiocarbamide, $C_3H_7 \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_{10}H_7$.

Little heat was evolved on mixing the constituents, but solid matter soon began to deposit; when this was complete, the yield was found to be over 90 per cent. of that theoretically obtainable. Recrystallisation from boiling spirit afforded a lustrous, almost pure white mass of fine needles, odourless, and melting, without decomposition, at 167.5 — 168.5° (corr.).

Analytical data.

0.2011 gave 0.1752 $BaSO_4$. $S = 11.97$.

$C_{13}H_{16}N_2SO$ requires $S = 11.77$ per cent.

The compound is insoluble in water, moderately soluble in boiling alcohol, rather sparingly in cold; the latter solution is desulphurised at once by ammoniacal, and gradually by neutral, silver nitrate. It is very freely soluble in chloroform, easily in hot benzene, moderately in cold; the benzene solution is precipitated by light petroleum. Warm dilute caustic alkali dissolves the substance to a moderate extent, the solution behaving with hydrochloric acid or with alkaline lead tartrate in a manner similar to that of the corresponding phenyl derivative.

III. PHENACETYLTHIOCARBIMIDE, $C_6H_5 \cdot CH_2 \cdot CO \cdot NCS$, AND ITS DERIVATIVES.

Phenylacetic acid dissolved in dry chloroform was mixed with phosphorus pentachloride, the hydrogen chloride driven off on the water bath, and the residue distilled, most of the chloride coming over at 92° under a pressure of 11 mm. It was then mixed with dry benzene and lead thiocyanate, the latter in somewhat greater proportion than that required by the equation

the mixture boiled until the solution was free from chlorine (which occupied about 10 minutes), and then filtered, well washed, and diluted with more benzene to 1 gram mol. per litre, assuming quantitative interaction.

The solution thus obtained had a pale yellowish colour, a distinct, but not very strong acid thiocarbimide odour, and attacked the eyes only slightly. In contact with water, it decomposed gradually in the cold, or rapidly on warming, with production of thiocyanic acid,

but gave the ordinary thiocarbimide reaction (desulphurisation) with alkaline lead or ammoniacal silver solutions—in both cases on warming. This benzene solution was employed in preparing the following derivatives.

ab-Phenacetylphenylthiocarbamide, $C_6H_5 \cdot CH_2 \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5$.

Molecular proportions of aniline in alcohol and the thiocarbimide in benzene were mixed; there was considerable disengagement of heat, and a brownish, clear liquid resulted, from which, on concentration, solid matter was deposited; after washing with spirit, the latter formed a nearly white, crystalline powder, amounting to about 80 per cent. of that theoretically obtainable, according to the equation

and reckoned as before on the amount of chloride employed. The solid was twice recrystallised from spirit, and thereby obtained in tufts of lustrous white prisms melting at $109-110^\circ$ (corr.). A sulphur determination afforded the following result.

0.2026 gave 0.1718 $BaSO_4$. $S = 11.65$.

$C_{15}H_{14}N_2SO$ requires $S = 11.86$ per cent.

Phenacetylphenylthiocarbamide melts when boiled with water, in which, however, it is practically insoluble; the fused substance floats as an oil, which, on cooling, solidifies to a radiating, crystalline cake. It is freely soluble in ether and in boiling alcohol, but only sparingly in cold; very freely in chloroform and benzene. The solution in weak spirit gives no colour reaction with ferric chloride; it is desulphurised easily by boiling with alkaline lead tartrate, and is blackened instantly in the cold by ammoniacal silver nitrate.

Action of Silver Nitrate.—A quantity of the pure thiocarbamide dissolved in a considerable volume of boiling spirit was mixed with a little more than the calculated amount of silver nitrate in weak alcohol. Silver sulphide was immediately precipitated, and, after a few minutes' boiling, was filtered off; the brownish filtrate at once began to deposit crystals and shortly became solid. By recrystallisation, the *urea* was obtained in long, thin, white needles, which become electrical on friction, and melt at $168-169^\circ$ (corr.).

A nitrogen determination yielded the following data.

0.2009 gave 19.8 c.c. at 17° and 752 mm. $N = 11.30$.

$C_{15}H_{14}N_2O_2$ requires $N = 11.05$ per cent.

The substance is insoluble in water; it dissolves, but not very freely, in boiling alcohol, from which, on cooling, it separates almost completely; it is rather sparingly soluble in ether, easily in hot benzene, very freely in chloroform. Prepared as above, the yield was about three-fourths of the theoretical.

ab-Phenacetylorthotolylthiocarbamide,
 $C_6H_5 \cdot CH_2 \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_4 \cdot CH_3$.

A practically quantitative yield of this substance was obtained, with marked evolution of heat, on mixing the thiocarbimide and ortho-

toluidine, in benzene and spirit respectively. When recrystallised from boiling alcohol, it occurred in beautiful, vitreous prisms, devoid of colour, and melting at 149—150° (corr.). It was dried over sulphuric acid and analysed.

0.2186 gave 0.1834 BaSO₄. S = 11.53.

C₁₆H₁₆N₂SO requires S = 11.28 per cent.

This thiocarbamide is insoluble in water, rather sparingly soluble in boiling alcohol, very sparingly in cold. Silver salts when added to its alcoholic solution, at once precipitate silver sulphide; with alkaline lead tartrate desulphurisation occurs moderately easily on boiling; if the latter process be carried out in potash instead of alcoholic solution, the tube becomes plated with a brilliant speculum of galena.

Action of Silver Nitrate.—By acting with silver nitrate in boiling alcoholic solution, as described above, the filtrate, on cooling, deposited 76 per cent. of the theoretical yield of *phenacetylorthotolylurea*. When recrystallised from alcohol, it formed tangled wisps of silky, flexible needles melting at 161.5—162° (corr.).

0.201 gave 18.4 c.c. of moist nitrogen at 15° and 755 mm. N=10.64.

C₁₆H₁₆N₂O₂ requires N = 10.47 per cent.

The compound is insoluble in water, rather sparingly soluble in boiling alcohol, and very sparingly in cold. Like all its congeners of the phenacetyl class hitherto obtained, it separates from alcohol in a very bulky condition, a quite insignificant quantity when dissolved in the hot liquid, causing the whole mass on cooling to solidify.

ab-Phenacetylparatolylthiocarbamide,

Heat was evolved from the constituents when mixed, and on cooling and stirring the clear brownish solution, fine, vitreous crystals presently began to separate; they were drained, well washed, recrystallised from boiling alcohol, and thus obtained in brilliant, rhombic plates, which, when seen in mass, had a very faint yellow tinge, and melted at 150—151° (corr.).

The formula was checked by analysis.

0.1985 gave 0.1590 BaSO₄. S = 11.01.

C₁₆H₁₆N₂SO requires S = 11.28 per cent.

The compound is slowly and rather sparingly soluble in boiling alcohol or benzene, insoluble in water; with lead and ammoniacal silver salts, it behaves like the corresponding ortho-derivative.

Action of Silver Nitrate.—By treating the boiling alcoholic solution,

which should be dilute, with the above reagent, *ab-phenacetylparatolylurea* was obtained. When recrystallised from alcohol, in which it is rather sparingly soluble even at the boiling point, it formed long, hair-like, flexible, white needles, insoluble in water, nearly so in cold spirit, and melting at 189—189·5° (corr.).

Analytical data :—

0·2024 gave 18·4 c.c. at 12° and 759 mm. N = 10·78.

C₁₆H₁₆N₂O₂ requires N = 10·47 per cent.

Prepared as before, using alcoholic benzyaniline; the resultant clear, pale brown liquid after two days' standing showed no sign of crystallisation, but, on pouring out from the containing flask into a dish, it at once solidified to a mass of fine needles; the yield was almost quantitative. By recrystallisation from hot benzene, microscopic prisms were obtained, possessing, when seen in mass, a faint lemon-yellow tinge, and melting at 127·5—128·5° (corr.) with decomposition.

0·2014 gave 0·1348 BaSO₄. S = 9·20.

C₂₂H₂₆N₂SO requires S = 8·90.

The compound is insoluble in water, rather sparingly soluble in ether or boiling alcohol, much less so in cold, easily in hot benzene or acetone, very freely in chloroform. Its alcoholic solution is almost neutral; if mixed with silver nitrate, a creamy-white precipitate forms, and the liquid becomes sharply acid; this precipitate (or that produced by the addition of ammoniacal silver nitrate) is not blackened by boiling, neither is the thiourea desulphurised by boiling with alkaline lead tartrate.

Phenacetylthiocarbimide and Ammonia.

The former, in benzene, was mixed with a considerable excess of alcoholic ammonia; much heat was evolved, and, on cooling, large, ice-like, colourless plates were deposited. They were free from sulphur, moderately easily soluble in hot water, sparingly in cold, more freely in alcohol, and melted at 156—157°. The warm solution readily dissolved freshly precipitated yellow oxide of mercury, and on cooling a white solid was deposited, melting at 207·5—208·5°. Consequently, the product was not the expected phenacetylthiourea, but phenylacetamide,* formed, probably, in the following manner

* CH₂Ph·CO·NH₂ melts at 158°; its HgO compound (Reimer, *Ber.*, 1880, **13**, 741) at 208°.

This action is by no means exceptional; thus Miquel (*Bull.*, **25**, 104), by passing dry ammonia into an ethereal solution of acetylthiocarbimide, obtained, instead of acetylthiourea, an oil (which he thought might possibly be acetamide thiocyanate); moreover, succinyldithiocarbimide, when treated with alcoholic ammonia, yielded (*Trans.*, 1895, **67**, 573) succinamide; and propionylthiocarbimide (*ante*), under similar conditions, gave a brownish oil, from which no thiourea could be isolated.

Other Acidic Thiocarbimides.—Several attempts were made to obtain from picryl chloride the corresponding picrylthiocarbimide, $C_6H_2(NO_2)_3 \cdot NCS$. Both lead and mercuric thiocyanates were employed, and as solvents, benzene, toluene, or cumene; but, under no circumstances, was there any indication of the desired union.

Experiments with the chlorides of phenylsulphonic and ethylsulphuric acids are now in progress, the results of which, if successful, will be communicated later on.

In conclusion, I wish to express my thanks to Mr. R. E. Doran for the help which he has given with a portion of the work above recorded.

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