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CLXXXII.—*Studies in the Camphane Series. Part XXIV. Camphoryldithiocarbamic Acid and Camphorylthiocarbimide.*

By Martin Onslow Forster and Thomas Jackson.

When bornylcarbimide was obtained by the action of nitrous acid on bornylcarbamide (Forster and Attwell, Trans., 1904, **85**, 1188), it was hoped that the resolution of racemic alcohols might be effected by converting these into a mixture of carbamates, separable by fractional crystallisation, but the comparative indifference of bornylcarbimide towards alcohols precludes its application to this problem. Since then, however, Pickard and Littlebury (Trans., 1906, **89**, 467) have accomplished the division of racemic α-phenyl-α′-4-hydroxyphenylethane by means of *l*-menthylcarbimide, and it is probable that *d*-camphorylcarbimide (Forster and Fierz, Trans., 1905, **87**, 110) could be used for a similar purpose, as it has the property of yielding urethanes with simple alcohols. The production of these carbimides, however, presents certain difficulties, and it seemed desirable to ascertain whether an optically active thiocarbimide could not be prepared more readily, and applied for the purpose indicated. Unsuccessful experiments with this object had been made with bornyl-

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amine (Forster and Attwell, *loc. cit.*), and we therefore proceeded to study the possibilities of aminocamphor in the hope that dicamphoryl-thiocarbamide might be made to yield camphoryl mustard oil by a process analogous to the well-known transformation of diphenylthio-carbamide into phenylthiocarbimide.

On heating an ethereal solution of aminocamphor with carbon disulphide, however, we were surprised to find that hydrogen sulphide is not set free, owing to the remarkable stability of camphoryl-dithiocarbamic acid, $C_8H_{14}\begin{cases}CH\cdot NH\cdot CS\cdot SH\\ CO\end{cases}$. The usual result of treating an aliphatic amine with carbon disulphide is the formation of alkylamine alkyldithiocarbamate, which gradually breaks up into dialkylthiocarbamide and hydrogen sulphide,

$$CS_2 + 2X\cdot NH_2 = SC\begin{cases}NHX\\ SH,NH_2X\end{cases} = SC\begin{cases}NHX\\ NHX\end{cases} + H_2S,$$

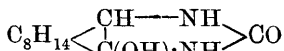
and this is the course which bornylamine follows. In the aromatic series, the intermediate stage is not observed, aniline phenyldithio-carbamate, for instance, losing hydrogen sulphide too quickly to permit of its being isolated, although Losanitsch (*Ber.*, 1891, **24**, 3021; 1907, **40**, 2970) has shown that if the action of carbon disulphide on aniline is conducted in presence of ammonia, elimination of hydrogen sulphide may be arrested, and the ammonium salt of phenyldithiocarbamic acid produced. The literature shows that a variety of aliphatic amines have been treated with carbon disulphide, but in no case, so far as we have been able to ascertain, has the dithiocarbamic acid been isolated; the aromatic representatives, also, would appear to be most unstable, phenyldithiocarbamic acid, for example, having been described as changing immediately into thio-carbanilide, hydrogen sulphide, and carbon disulphide (Rathke, *Ber.*, 1878, **11**, 958).

The stability of camphoryldithiocarbamic acid appears therefore to be unique, and the nearest approach to its properties is furnished by phenyldithiocarbazinic acid, $C_6H_5\cdot NH\cdot NH\cdot CS\cdot SH$, the phenylhydrazine salt of which was described by E. Fischer (*Annalen*, 1878, **190**, 115). Busch records a definite melting point for the free acid (*Ber.*, 1895, **28**, 2639), but Busch and Ridder (*Ber.*, 1897, **30**, 845) describe the substance as somewhat unstable, in part changing into phenyl-hydrazine phenyldithiocarbazinate, whilst the remainder undergoes a more profound decomposition and becomes black. No change of this character has been observed in connexion with camphoryldithio-carbamic acid, a colourless, crystalline specimen of which has now been exposed to diffused light during more than six months without altering in appearance or developing any odour. In speculating as to

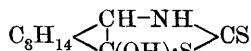
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the cause of this stability, we were naturally led to ascribe it to the neighbourhood of the carbonyl group, and, in view of the isomerism observed in connexion with camphorylcarbamide (Forster and Fierz, *loc. cit.*), considered the possibility of representing it as a pseudo-modification of the normal dithiocarbamic acid:

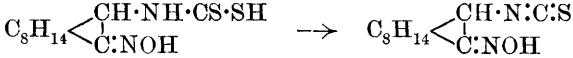


Camphoryl-ψ-carbamide.

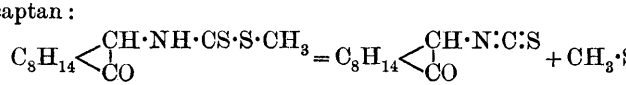


Camphoryl-ψ-dithiocarbamic acid.

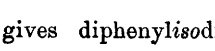
For several reasons, however, this explanation appears most unlikely. In the first place, the substance is a strong acid, and also differs from camphoryl-ψ-carbamide in its failure to yield a nitroso-derivative. Furthermore, the oxime of camphoryldithiocarbamic acid, prepared by the action of carbon disulphide on aminocamphoroxime, although capable of a separate existence, readily loses hydrogen sulphide, passing into the oxime of camphorylthiocarbimide:



Finally, the methyl ester of camphoryldithiocarbamic acid, a colourless substance melting sharply at 147° without liberating gas, breaks up at about 170°, yielding camphorylthiocarbimide and methyl mercaptan:



We conclude therefore that the stability of camphoryldithiocarbamic acid is merely another manifestation of the remarkable influence exerted by the carbonyl radicle upon the functions of a group attached to the neighbouring carbon atom, and in this association the behaviour of other aminoketones towards carbon disulphide might repay investigation.

Another interesting distinction from the dithiocarbamic acids, derivatives of which have been described hitherto, is to be found in the power displayed by the camphoryl derivative to yield a benzoyl compound. Numerous alkyl esters of dithiocarbamic acids have been prepared, even from the unstable compounds of the aliphatic and aromatic series, but the action of benzoyl chloride on the acids has either not been studied, or has led to negative results. In the case of phenyldithiocarbamic acid, Busch and Becker, who described definite ethyl and benzyl esters (*J. pr. Chem.*, 1899, [ii], **60**, 217), state that the benzoyl derivative cannot be isolated, as it loses water immediately, and gives diphenyl*iso*dithiodiazolone, , along with *s*-dibenzoylphenylhydrazine. From camphoryldithiocarbamic acid and benzoyl chloride in ether, however, we have obtained a well-

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defined benzoyl derivative which may be recrystallised; nevertheless, it is easily decomposed into camphorylthiocarbimide and, presumably, thiobenzoic acid, and the mustard oil alone is isolated if the benzoylation of camphoryldithiocarbamic acid is attempted under ordinary conditions in presence of alkali.

The action of nitrous acid on the dithiocarbamic acid, although leading ultimately to the mustard oil, is not quite so simple as would appear from the equation :

$$C_8H_{14}\begin{cases}CH\cdot NH\cdot CS\cdot SH\\ CO\end{cases} + 2HNO_2 = C_8H_{14}\begin{cases}CH\cdot N{:}C{:}S\\ CO\end{cases} + S + 2NO + 2H_2O.$$

There is evidence that an intermediate product of oxidation is first formed without loss of sulphur, because an ethereal solution of camphoryldithiocarbamic acid, when mixed with amyl nitrite, develops a dark brown coloration, and deposits colourless prisms consisting of the substance :

$$C_8H_{14}\begin{cases}CH\cdot N\text{—}C{:}S\\ CO\end{cases}\quad \text{or} \quad C_8H_{14}\begin{cases}CH\cdot N{:}C\begin{cases}S\\ S\end{cases}\\ CO\end{cases},$$

unmixed with sulphur; the product may be recrystallised from cold solvents, but, if the temperature is raised, breaks up into camphorylthiocarbimide and sulphur. It may be noted as a curious point that, whilst the specific rotatory power of the oxidation product is $[\alpha]_D$ 102°, the thiocarbimide is lævorotatory, having $[\alpha]_D$ −114°.

The investigation of camphoryldithiocarbamic acid has brought to light a variety of methods by which the mustard oil may be obtained from it. Two of these have already been mentioned, and a third is the normal decomposition of the mercuric salt when warmed with alcoholic ammonia; a less usual one consists in mixing pyridine solutions of the dithiocarbamic acid and benzoyl chloride, and in attempting to prepare the benzenesulphonic derivative it was found that the thiocarbimide is produced almost quantitatively when an alkaline solution of the dithiocarbamate is agitated with benzenesulphonic chloride. A sixth process depends on the behaviour of camphorylthiocarbamide towards nitrous acid, which does not give rise to a nitroso-derivative, thus classifying the thiocarbamide with camphorylcarbamide instead of with the pseudo-modification.

It does not appear probable that the mustard oil will prove serviceable in the task of resolving racemic alcohols, its reaction with the hydroxyl group being sluggish; methyl camphorylthiocarbamate was obtained when the factors were heated at 150° during five hours. The behaviour of the thiocarbimide towards phenylhydrazine is

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interesting, however, and three definite products have been isolated, two of which have the empirical formula of a camphorylphenylthiosemicarbazide, whilst the third is evidently an internal anhydride or phenylhydrazone. The work of A. E. Dixon (Trans., 1892, **61**, 1012) and of Marckwald (*Ber.*, 1892, **25**, 3098; 1899, **32**, 1081) has shown that many of the thiosemicarbazides produced from aromatic thiocarbimides and hydrazines exist in two modifications, which Busch and Holzmann (*Ber.*, 1901, **34**, 320) have proved to be structurally distinct (compare also Busch, Opfermann, and Walther, *Ber.*, 1904, **37**, 2318). Owing to lack of material, our examination of the camphorylphenylthiosemicarbazides has not been so complete as that of the authors mentioned, but we believe them to be α- and β-derivatives of phenylhydrazine respectively, as represented by the formulæ:

$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CS\cdot N(C_6H_5)\cdot NH_2\\ |\\ CO\end{matrix}$ and

M. p. 183°.

$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CS\cdot NH\cdot NH\cdot C_6H_5\\ |\\ CO\end{matrix}$;

M. p. 163°.

the modification melting at 183° readily passes into the anhydride, which most probably has the constitution:

$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CS\\ |\\ C:N\text{——}N\cdot C_6H_5\end{matrix}.$$

Although the two thiosemicarbazides have almost the same specific rotatory power, the colours which they develop with sulphuric acid, copper acetate, ferric chloride, bleaching powder, nickel acetate, and ammoniacal silver oxide render it a simple matter to distinguish between the isomeric forms, and to differentiate these from the anhydride. We have not been able to transform the α-derivative into the isomeride by boiling the alcoholic solution with a small quantity of hydrochloric acid (compare Marckwald, *loc. cit.*), because this treatment gives rise to the anhydride, but we have shown that, under the same conditions, the β-modification is not converted into the less fusible form.

Experimental.

Camphoryldithiocarbamic Acid, $C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CS\cdot SH\\ |\\ CO\end{matrix}$.

One hundred grams of *iso*nitrosocamphor were reduced in alkaline solution with zinc dust, and the aminocamphor, after extraction with ether, was converted into the hydrochloride and reprecipitated by alkali; the solution in ether was then dried with solid potassium hydroxide, immersed in cold water, and slowly mixed with 48 grams of carbon disulphide. Heat was developed, and when action was complete the

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solvent was evaporated until about 200 c.c. of liquid remained; as this product cooled, it solidified to a crystalline cake which, when drained on earthenware, weighed 110 grams instead of 134. The substance was recrystallised from methyl alcohol, forming glistening, hexagonal plates which melt and decompose at 128°:

0·2337 gave 12·1 c.c. of nitrogen at 18° and 755·5 mm. N = 5·94.
0·1003 „ 0·1939 $BaSO_4$. S = 26·50.
$C_{11}H_{17}ONS_2$ requires N = 5·77; S = 26·33 per cent.

The yield of dithiocarbamic acid is not impaired when the ethereal solution of aminocamphor is heated with carbon disulphide in a reflux apparatus during many hours, but, if solvents of higher boiling point are used, hydrogen sulphide is liberated slowly, and the normal change into disubstituted thiocarbamide takes place. In recrystallising the substance, therefore, it is advisable to proceed as rapidly as possible, and to deal with moderate quantities; although cold chloroform dissolves it sparingly, an attempt to recrystallise 50 grams from this medium failed, owing to the necessity of boiling it with the solid for some minutes, the filtered liquid depositing no crystals on cooling, and yielding a gummy residue from which dicamphorylthiocarbamide alone was obtainable. Cold acetone or ether and hot methyl and ethyl alcohols dissolve the dithiocarbamic acid freely, forming supersaturated solutions; hot benzene dissolves it sparingly, and it is practically insoluble in boiling light petroleum. The substance is a pronounced acid, dissolving in sodium carbonate and cold dilute caustic alkalis without change, but hot alkalis transform it into dicamphorylthiocarbamide.

A solution containing 0·2614 gram in 25 c.c. of acetone gave α_D 0°27′ in a 2-dcm. tube, whence $[\alpha]_D$ 21·5°; on exposing this liquid to light during several days, it became yellow and lævorotatory to the extent of α_D 0°45′, indicating transformation into camphorylthiocarbimide (see below). A 2 per cent. solution of the dithiocarbamic acid in potassium hydroxide is inactive, and remains so when heated at 90° during several days, when the pale yellow liquid gradually becomes green without depositing dicamphorylthiocarbamide, although this is precipitated on acidification. An alcoholic solution giving α_D 18′ when freshly prepared increased in optical activity to α_D 1°0′ after three months, sulphur separating in well-defined crystals. An ethereal solution of the acid develops a deep brown coloration with ferric chloride, but there is no change when sodium nitroprusside is added to a solution in alcohol or dilute ammonia.

Behaviour towards Metallic Salts.—When alcoholic copper acetate is added to a moderately concentrated solution of camphoryldithiocarbamic acid in the same solvent, a deep brown coloration is developed

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but there is no precipitate until copper is in excess, when a pale brown derivative appears; on warming this compound in the liquid, it becomes faintly yellow and highly insoluble. Alcoholic silver nitrate develops a deep yellow colour, the liquid remaining clear, but on adding a few drops of alcoholic ammonia a pale brown precipitate is formed, sparingly soluble in boiling alcohol; excess of alcoholic ammonia dissolves this material, and the solution may be boiled without precipitating silver sulphide. Lead acetate forms a bulky, pale yellow salt, which, when boiled with alcohol, deposits lead sulphide in the form of a mirror. A solution of mercuric chloride in alcohol yields a bulky, snow-white precipitate which does not change in appearance when the liquid is boiled. If the solution of camphoryldithiocarbamic acid is faintly ammoniacal, however, the precipitate with alcoholic mercuric chloride is yellow, and quickly becomes black on boiling, whilst the filtered liquid yields crystals of camphorylthiocarbimide.

Methyl Camphoryldithiocarbamate, $C_8H_{14}\begin{cases}CH\cdot NH\cdot CS\cdot S\cdot CH_3\\ CO\end{cases}$.

Camphoryldithiocarbamic acid combines with methyl iodide very readily, hydrogen iodide being eliminated when the two materials are warmed together. Twenty grams of the acid were dissolved in absolute methyl alcohol containing 2 grams of sodium, and treated with 15 grams of methyl iodide; the deep yellow colour faded, and, after a few minutes on the steam-bath, water was added, the crystalline precipitate being then filtered quickly and washed with cold water. While the substance remained moist, it retained the offensive odour of methyl mercaptan, but this was gradually lost in the desiccator, and on recrystallising the dry material from boiling petroleum, in which it dissolves readily, silky, centimetre-long needles were obtained quite odourless, and melting at 147° without evolving gas:

0·2005 gave 9·6 c.c. of nitrogen at 16° and 765 mm. N = 5·62.

0·0957 ,, 0·1730 $BaSO_4$. S = 24·78

$C_{12}H_{19}ONS_2$ requires N = 5·45; S = 24·90 per cent.

A solution containing 1·0450 grams in 25 c.c. of chloroform gave α_D 9°35′ in a 2-dcm. tube, whence $[\alpha]_D$ 114·6°. The ester is freely soluble in chloroform, benzene, acetone, ether, or ethyl acetate, less readily in methyl and ethyl alcohols; it is very sparingly soluble in cold petroleum, and an ethereal solution gives no colour with ferric chloride.

Decomposition by Heat.—When warmed with water, the odour of methyl mercaptan quickly becomes perceptible, followed by the pungent vapour of camphorylthiocarbimide rising with the steam.

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Five grams of the dry ester were mixed with clean, white sand in a small distilling flask connected with a double U-tube immersed in a freezing mixture, the apparatus having been carefully dried, and closed by a tube of calcium chloride. The flask was heated in an oil-bath at 170° during two hours, when approximately 1 c.c. of methyl mercaptan collected in the receiver; this product was identified by conversion into the mercury compound, which melted at 177° after crystallisation from alcohol. The residue in the flask was recognised as camphoryl-thiocarbimide.

Benzoyl Derivative of Camphoryldithiocarbamic Acid,

$$C_8H_{14}\begin{cases}CH\cdot NH\cdot CS\cdot S\cdot CO\cdot C_6H_5\\ CO\end{cases}.$$

On attempting to benzoylate camphoryldithiocarbamic acid under the familiar conditions of the Schotten-Baumann process, it was found that camphorylthiocarbimide is the main product. Experiments in which benzoyl chloride acted on the acid dissolved in pyridine gave distinct evidence of the formation of a benzoyl derivative, for, on dissolving the well-washed product in alcohol, ethyl benzoate was recognisable in the liquid, although it was the thiocarbimide which crystallised on cooling. Even when the material arising by benzoylation in pyridine is dried as quickly as possible without heating, and recrystallised from petroleum to exclude water, the benzoyl derivative is mixed with camphorylthiocarbimide, but an individual substance may be obtained by employing ether as a medium.

Ten grams of camphoryldithiocarbamic acid were dissolved in 100 c.c. of dried ether and mixed with 6 grams of benzoyl chloride; on evaporating the solvent in a current of dry air, clusters of yellow needles separated, and on recrystallisation from warm petroleum, in which it is moderately soluble, the benzoyl derivative was obtained in long, colourless, silky needles melting at 105°:

0·2690 gave 9·2 c.c. of nitrogen at 20° and 762·5 mm. N = 3·92.

0·0994 ,, 0·1357 $BaSO_4$. S = 18·74.

$C_{18}H_{21}O_2NS_2$ requires N = 4·03; S = 18·44 per cent.

A solution containing 0·2865 gram in 25 c.c. of chloroform gave α_D 1°12′ in a 2-dcm. tube, whence $[\alpha]_D$ 52·3°. The benzoyl derivative is freely soluble in chloroform, benzene, acetone, and ethyl acetate, less readily in methyl and ethyl alcohols, solutions in these media depositing camphorylthiocarbimide on cooling; even when petroleum is employed, there is danger of decomposing the benzoyl derivative, and it is only by operating with small quantities, and cooling the liquid as rapidly as possible, that a specimen of the benzoyl derivative unmixed with thiocarbimide can be obtained.

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Action of Amyl Nitrite on Camphoryldithiocarbamic Acid.

In preparing camphorylthiocarbimide by the action of nitrous acid on camphoryldithiocarbamic acid (see below), various indications suggested the formation of an intermediate compound which passed into the mustard oil with loss of sulphur, and this material was ultimately isolated in the following manner.

Camphoryldithiocarbamic acid was dissolved in dry ether and mixed with an equal weight of amyl nitrite, which immediately developed a dark reddish-brown coloration, followed by continuous evolution of red gas; as the effervescence proceeded, the colour of the liquid gradually disappeared and colourless prisms separated. Attempts to recrystallise this material led at first to the thiocarbimide with elimination of sulphur, but on dissolving the substance in chloroform and adding petroleum, colourless crystals were obtained which become yellow at about 110°, melting and decomposing at 116°:

0·3287 gave 16·4 c.c. of nitrogen at 20° and 755 mm. N = 5·67.
0·0936 ,, 0·1776 $BaSO_4$. S = 26·05.

$C_{11}H_{15}ONS_2$ requires N = 5·81; S = 26·55 per cent.

The formulæ $C_{11}H_{15}ONS_2$ and $C_{22}H_{32}O_2N_2S_4$ being indistinguishable by analysis, determinations of molecular weight were made in benzene and in phenol. In the former solvent, the results were abnormal, averaging about 700, but in phenol an average of 227 was obtained, corresponding with the simpler formula $C_{11}H_{15}ONS_2$, which requires 241, whilst $C_{22}H_{32}O_2N_2S_4$ amounts to 484. A solution containing 0·3072 gram in 25 c.c. of chloroform gave α_D 2°30′ in a 2-dcm. tube, whence $[\alpha]_D$ 101·7°. The substance is freely soluble in chloroform or benzene, but dissolves less readily in acetone or ethyl acetate; methyl and ethyl alcohols dissolve it sparingly, and it is practically insoluble in light petroleum.

Camphorylthiocarbimide (*Camphoryl Mustard Oil*),

$$C_8H_{14}\begin{cases}CH\cdot N:C:S\\ CO\end{cases}$$

Twenty grams of camphoryldithiocarbamic acid were dissolved in 50 c.c. of pyridine, cooled with ice, and mixed with 12 grams of benzoyl chloride, also dissolved in pyridine; the temperature rose, and pyridine hydrochloride separated. After ten minutes, ice-water was added, the oily precipitate quickly becoming solid; this was drained on earthenware and boiled with alcohol containing a small proportion of water, the hot liquid depositing 17 grams of thiocarbimide as it cooled. The following alternative method was also satisfactory.

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Twenty c.c. of concentrated hydrochloric acid were added to 10 grams of camphoryldithiocarbamic acid dissolved in 200 c.c. of absolute alcohol, the ice-cold liquid being then treated with 5 grams of sodium nitrite in the minimum quantity of water. The first portions of the salt developed an intense brown coloration in the liquid, and a colourless precipitate was formed; this was collected after two hours, digested with warm absolute alcohol, and the solution filtered from sulphur and sodium chloride. On adding water, the thiocarbimide was precipitated, and, when recrystallised from a small quantity of hot absolute alcohol, separated in long, lustrous prisms which melt at 106·5°:

0·1804 gave 10·4 c.c. of nitrogen at 20° and 771·5 mm. N = 6·70.
0·1068 ,, 0·1174 $BaSO_4$. S = 15·07.

$C_{11}H_{15}ONS$ requires N = 6·70; S = 15·31 per cent.

A solution containing 0·2263 gram in 25 c.c. of absolute alcohol gave α_D −2°4′ in a 2-dcm. tube, whence $[\alpha]_D$ −114·1°; after several weeks, the activity of the solution almost disappeared, becoming stationary at α_D −0°5′. The mustard oil is readily soluble in benzene, and moderately so in alcohol; petroleum dissolves it readily when boiled, depositing lustrous, silky needles on cooling. It is insoluble in water, and the vapour in steam has a pungent odour which recalls that of camphorylcarbimide rather than phenyl mustard oil; boiling water and alkalis convert it slowly into dicamphorylthiocarbamide. Although sluggish in its action on water and alcohols, it reacts readily with ammonia and amines, yielding the following typical derivatives.

Camphorylthiocarbamide, $C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CS\cdot NH_2\\ |\\ CO\end{matrix}$, prepared by passing dry ammonia into a solution of the thiocarbimide in chloroform, separated on adding petroleum as an oil which rapidly solidified; when recrystallised from boiling water, it formed slender laminæ with silky lustre, and melted at 180°, evolving gas:

0·2078 gave 22·1 c.c. of nitrogen at 15·5° and 764 mm. N = 12·49.

$C_{11}H_{18}ON_2S$ requires N = 12·41 per cent.

A solution containing 0·2640 gram in 25 c.c. of chloroform gave α_D −0°57′ in a 2-dcm. tube, whence $[\alpha]_D$ −44·9°. The substance dissolves readily in cold alcohol, and is moderately soluble in boiling water and in hot benzene, but is practically insoluble in petroleum. With nitrous acid, it gives the thiocarbimide, behaving in this respect like camphorylcarbamide (Trans., 1905, **87**, 118).

Camphorylpiperidylthiocarbamide, $C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CS\cdot NC_5H_{10}\\ |\\ CO\end{matrix}$, was produced when the thiocarbimide, dissolved in a small proportion of

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benzene, was mixed with piperidine; heat was developed, and, after an interval, petroleum was added, the precipitated piperidyl derivative being then dissolved in dilute hydrochloric acid, filtered from a small quantity of dicamphorylthiocarbamide, and again precipitated with potassium hydroxide. Recrystallisation from alcohol gave well-formed, rhombic prisms melting at 188°:

0·1047 gave 0·0853 $BaSO_4$. S = 11·17.

$C_{16}H_{26}ON_2S$ requires S = 10·88 per cent.

A solution containing 0·3130 gram in 25 c.c. of chloroform gave α_D 0°40′ in a 2-dcm. tube, whence $[\alpha]_D$ 26·6°. The substance is freely soluble in chloroform or pyridine, readily in benzene or acetone, and moderately in methyl alcohol or ethyl acetate, from which it crystallises in transparent prisms; boiling petroleum dissolves it sparingly, however, and it separates from this medium in lustrous, silky needles.

Dicamphorylthiocarbamide, $C_8H_{14}\begin{cases}CH\cdot NH\cdot CS\cdot NH\cdot C_{10}H_{15}O\\ CO\end{cases}$, is obtained by the action of water, acids, and alkalis on the thiocarbimide, and crystallises from alcohol in colourless, glistening plates resembling thiocarbanilide; it melts at 176°:

0·2050 gave 12·75 c.c. of nitrogen at 16·5° and 780 mm. N = 7·43.

0·1050 ,, 0·0639 $BaSO_4$. S = 8·34.

$C_{21}H_{32}O_2N_2S$ requires N = 7·44; S = 8·51 per cent.

A solution containing 0·4832 gram in 25 c.c. of acetone gave α_D 2°6′ in a 2-dcm. tube, whence $[\alpha]_D$ 54·3°. The substance is readily soluble in chloroform, acetone, or glacial acetic acid, but only moderately in ether, ethyl acetate, methyl alcohol, or benzene; it is insoluble in cold petroleum, but dissolves very sparingly on boiling. When ethereal ferric chloride is added to a solution of the thiocarbamide in ether, no change is noticeable at first, but a pale brown, flocculent precipitate separates in the course of a few minutes.

Unlike thiocarbanilide, dicamphorylthiocarbamide is insoluble in alkalis; it is also insoluble in dilute acids, and resists the action of concentrated hydrochloric acid. It appears to be capable of undergoing transformation into a pseudo-modification, because a solution of camphoryldithiocarbamic acid in excess of potassium hydroxide remains clear when heated at 90° during several hours, although dicamphorylthiocarbamide is insoluble in potassium hydrogen sulphide.

Methyl camphorylthiocarbamate, $_8H_{14}\begin{cases}CH\cdot NH\cdot CS\cdot O\cdot CH_3\\ CO\end{cases}$, is formed when the mustard oil is heated in a sealed tube during five hours at about 150° with absolute methyl alcohol; it displays a tendency to form supersaturated solutions in methyl alcohol, but

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may be conveniently recrystallised from petroleum, when it melts at 118°:

0·2268 gave 11·7 c.c of nitrogen at 17° and 764 mm. N = 6·02.

$C_{12}H_{19}O_2NS$ requires N = 5·81 per cent.

A solution containing 0·3645 gram in 25 c.c. of chloroform gave α_D 3°10′ in a 2-dcm. tube, whence $[\alpha]_D$ 108·6°. The substance is freely soluble in methyl and ethyl alcohols, chloroform, benzene, or ethyl acetate.

The Camphorylphenylthiosemicarbazides.

Camphorylthiocarbimide and phenylhydrazine interact very readily when brought together in moderately dilute solutions. A great number of experiments have been made with the object of determining the conditions favouring the production of each modification, but the two thiosemicarbazides appear to be formed simultaneously, and require to be separated by fractional crystallisation. The following two experiments are typical of many.

Eight grams of the thiocarbimide were dissolved in chloroform and treated with 5 grams of phenylhydrazine. When the solvent had evaporated spontaneously, the gummy residue was warmed with methyl alcohol, which caused crystals to separate on cooling; this product, weighing about 6 grams, was recrystallised from methyl alcohol, separating in thin, lustrous plates melting at 183°. The mother-liquors yielded a small proportion of the anhydride, melting at 235°, along with about 4 grams of needles, more freely soluble in methyl alcohol, and melting at 163°.

Nine grams of the thiocarbimide dissolved in 120 c.c. of ether, to which a small quantity of alcohol had been added, were cooled in ice, and treated with 6 grams of phenylhydrazine, also dissolved in ether; the liquid changed to a clear, tough jelly, which underwent but slight shrinkage during six hours. This was dissolved in 20—30 c.c. of hot alcohol and warmed until the ether was removed; 8 grams of the less fusible thiosemicarbazide were deposited from this solution, the mother-liquor yielding about 1 gram of the isomeride.

The *camphorylphenylthiosemicarbazide*,

$$C_8H_{14}\begin{<}\begin{matrix}CH\cdot NH\cdot CS\cdot N(C_6H_5)\cdot NH_2\\ |\\ CO\end{matrix}\end{>},$$

which melts at 183°, is obtained with comparative ease, owing to its relatively sparing solubility, but it has the inconvenient property of yielding a tough, transparent jelly when dissolved in ether, alcohol, or petroleum, a peculiarity which has been recently noticed by E. Fischer and Abderhalden (*Ber.*, 1907, **40**, 3558) in connexion with a substance, $C_7H_{12}O_2N_2$, obtained from elastin by hydrolysis. We have made experiments to ascertain the minimum of material which

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is capable of producing this jelly, and find that if the thiosemicarbazide is first dissolved in a small quantity of hot alcohol, and the solution diluted with petroleum, one part in 300 gives a tough, transparent jelly, which does not liquefy during twenty-four hours; after this period, however, the medium gradually becomes limpid, and the solid separates in well-defined crystals, which at first appear suspended in the jelly:

0·1986 gave 23·1 c.c. of nitrogen at 19° and 759 mm. N = 13·35.

0·1847 „ 0·1325 $BaSO_4$. S = 9·85.

$C_{17}H_{23}ON_3S$ requires N = 13·25; S = 10·09 per cent.

A solution containing 0·3153 gram in 25 c.c. of chloroform gave α_D 1°31′ in a 2-dcm. tube, whence $[\alpha]_D$ 59·5°. The substance is insoluble in aqueous alkali, and is readily converted into the anhydride, described below, when the alcoholic solution is heated with a small quantity of hydrochloric acid, or when an attempt is made to recrystallise the solid from glacial acetic acid. An estimation of the molecular weight in benzene gave an average of 338 units, the value calculated from the empirical formula $C_{17}H_{23}ON_3S$ being 317.

The *camphorylphenylthiosemicarbazide*,

$$C_8H_{14}\begin{cases}CH\cdot NH\cdot CS\cdot NH\cdot NH\cdot C_6H_5\\ CO\end{cases},$$

which melts at 163°, is produced in small quantities only, even under the most favourable conditions:

0·2270 gave 25·5 c.c. of nitrogen at 22° and 765 mm. N = 12·82.

0·1016 „ 0·0767 $BaSO_4$. S = 10·36.

$C_{17}H_{23}ON_3S$ requires N = 13·25; S = 10·09 per cent.

A solution containing 0·2134 gram in 25 c.c. of chloroform gave α_D 1°0′ in a 2-dcm. tube, whence $[\alpha]_D$ 58·5°. Although the degree of optical activity is almost identical with that of the isomeric substance, the following colour tests serve to distinguish between the two materials; to render the comparison more convenient, the various reactions are tabulated alongside with those of the anhydride:

	M. p. 163°.	M. p. 183°.	Anhydride.
Concentrated sulphuric acid.	Rich blue.	Deep yellow.	Colourless.
Alcoholic copper acetate.	Intense bluish-green.	Intense, but transient, brown.	Transient brown, less intense.
Alcoholic copper nitrate.	Intense blue.	Blue, less intense.	Grass-green.
Alcoholic nickel acetate.	Colourless at first, purple on warming.	Grass-green.	No change.
Ethereal ferric chloride.	No change.	Deep red.	No change.

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	M. p. 163°.	M. p. 183°.	Anhydride.
Alcoholic silver nitrate.	White opalescence, pale brown on boiling.	White opalescence, black on boiling.	No change, even on boiling.
Ammoniacal silver oxide.	Yellow coloration, becoming green; black precipitate on boiling.	White opalescence, intensifying to a brown precipitate on boiling.	Immediate yellow precipitate, which does not darken on boiling.
Bleaching powder solution.	Deep orange.	Pale yellow.	No change.

The *anhydride*, $C_8H_{14}\begin{cases}CH\cdot NH\cdot CS\\ C:N\text{——}N\cdot C_6H_5\end{cases}$, crystallises in small, lustrous needles melting at 235°:

0·2153 gave 26·8 c.c. of nitrogen at 20° and 762 mm. N = 14·28.

0·1007 ,, 0·0783 $BaSO_4$. S = 10·68.

$C_{17}H_{21}N_3S$ requires N = 14·04; S = 10·70 per cent.

A solution containing 0·2823 gram in 25 c.c. of chloroform gave α_D 6°12′ in a 2-dcm. tube, whence $[\alpha]_D$ 274·5°. The substance is sparingly soluble in methyl and ethyl alcohols, ethyl acetate, or benzene, more readily, however, in acetone and chloroform; it is freely soluble in pyridine, but practically insoluble in petroleum.

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