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ON THE ACTION OF ALKYL THIOCYANATES AND ALKYL ISOTHIOCYANATES WITH THIOL ACIDS.

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THE fact that dithiocarbamic esters are formed from alkyl thiocyanates and hydrogen sulphide led Chanlaroff[1] to examine the behavior of ethyl thiocyanate, C_2H_5SCN, with thioacetic acid, thioacetic anhydride, and thiobenzoic acid. He found, in each case, that the compounds reacted and that crystalline products resulted. However, he only described the addition product with thioacetic acid, and to this he assigned the formula $CH_3CONHCS.SC_2H_5$. He remarked, that this addition product behaved like a "molecular-verbindung" and that it showed such great instability in its reactions that all attempts to prepare a derivative from it, of any sort, were without success.

Numerous acyl dithiocarbamates of this type have been prepared by Dr. T. B. Johnson and ourselves, and we have found that derivatives can easily be prepared from the above and also from a large number of other acyldithiourethanes.

Our work has shown that thiocyanates, RSCN, readily react with thiol acids, on the steam-bath, in at least two ways. The

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[1] *Ber. d. chem. Ges.*, 15, 1987 [1882].

more commonly observed reaction is a direct addition as found by Chanlaroff:

I. $C_2H_5SCN + HSCOC_6H_5 = C_2H_5S.CSHNCOC_6H_5$.

Primary monothiocyanates, with aliphatic groups, as well as those prepared from benzyl, *p*-brom, *p*-nitrobenzyl, and *m*-xylyl halides, react almost entirely in this manner and very small amounts of by-product are formed. The di- and polythiocyanates appear to behave in a different manner and work on these is now in progress here.

Certain thiocyanates, even when the action is moderated by heating in the presence of benzene, react in a complicated manner. They evolve hydrogen cyanide and thiol esters result. The action apparently takes place in the following stages:

II. $C_6H_5SCN + HS.COC_6H_5 = C_6H_5S.COC_6H_5 + HNCS$.

The thiocyanic acid which is liberated then breaks down into hydrogen cyanide and other products.[1] Besides, it has been observed to react with thiobenzoic present in the following manner:

III. $HNCS + HS.COC_6H_5 = H_2NCOC_6H_5 + CS_2$.

The products are carbon disulphide and benzamide and the reaction is similar to that of hydrogen sulphide and thiocyanic acid when ammonia and carbon disulphide are obtained.[2]

In these latter reactions the products are, therefore, thiol esters, benzamide, hydrogen cyanide, and carbon disulphide; occasionally hydrogen sulphide is noticed, probably as a decomposition product of the thio acid, and in certain cases, especially when the reactions are performed without benzene, the above products are accompanied by thick oils, varnishes, or tars from which it is difficult to isolate anything solid in a state of purity.

The isothiocyanates, RNCS, or mustard oils react even more energetically with thio acids than the normal thiocyanates. When phenyl mustard oil or allyl mustard oil is warmed with thioacetic or thiobenzoic acid, a reaction takes place below the boiling-point of benzene, apparently in a quantitative manner as follows:[3]

IV. $RNCS + HS.COC_6H_5 = RNHCOC_6H_5 + CS_2$.

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[1] Peter Klason: *J. prakt. Chem.*, [2], 26, 57 (1887).

[2] Voelckel: Pogg. *Ann.*, **65**, 313 (1845).

[3] Since the above was written Eibner (*Ber. d. chem. Ges.*, **34**, 660) has published the surprising statement that phenyl mustard oil does not react with thioacetic acid on long heating in a tube at 100°. We find that the substances react at ordinary temperature.

This reaction is of the same nature as that of thiocyanic acid with hydrogen sulphide, thiobenzoic acid, etc., mentioned above. It is also analogous to that observed by Kay,[1] who found that phenyl mustard oil and benzoic acid gave carbon oxysulphide and benzanilide, although at a much higher temperature than that in the present experiments.

Not only the alkyl, but also the acyl, isothiocyanates behave in this manner. Benzoyl rhodanide, C_6H_5CONCS, and thiobenzoic acid, for example, gave off carbon disulphide and dibenzamide was isolated and identified.

The above reactions sharply distinguish the thiocyanates from the isothiocyanates, and when a rhodanide is heated with thiobenzoic acid, the non-formation of carbon disulphide may be considered as conclusive proof that an isothiocyanate or mustard oil form is not present. We have now applied these reactions to the examination of some compounds described as mustard oils.

Before entering on the discussion of this it may be well to state that when reactive organic halogen compounds are boiled with potassium thiocyanate, the first product formed appears, in all cases, to be a normal thiocyanate, R—SCN. When the group R is strongly negative[2] the product immediately undergoes a molecular rearrangement into the form RNCS[3] (when R is the group $C_6H_5CO—$, etc.).

Less negative groups, such as the allyl group,

$$CH_2{=}CH-CH_2-,$$

permit of the isolation of the primary product, allyl thiocyanate, if heating is avoided, otherwise allyl mustard oil is obtained. When, in other cases, a halide of the form $-CH_2X$ is employed the thiocyanates show the greatest stability. Methyl thiocyanate is only partially converted into mustard oil on heat-

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[1] *Ber. d. chem. Ges.*, **26**, 2848 (1893).

[2] Miquel : *Ann. chim. phys.*, (5), 11, 318 (1877) ; Dixon : *J. Chem. Soc.* (London), **75**, 388 (1899).

[3] The mechanism of this reaction or rearrangement appears to the writer to be as yet unexplained. The view accepted at present that the more negative the group, the more readily the rearrangement takes place (compare Michael : *J. prakt. Chem.*, **37**, 510 (1888), requires some modification, since data have already been collected that are not in accordance with this view. We hope to return to this subject at a later date. The methylene dissociation theory of Nef (*Ann. Chem.* (Liebig), 298, 370 (1897)) does not offer a simple explanation of the rearrangement which, in all probability, takes place in the case of acyl sulphocyanates. An attempt to prepare normal benzoyl thiocyanate, $C_6H_5CO.SCN$, by acting on potassium thiolbenzoate, suspended in benzene, with cyanogen bromide gave benzoyl disulphide as the chief product. W.

ing at a temperature of 180°–185°.[1] Recently, however, a number of cases have been described in which the grouping $—COCH_2X$ is said to yield mustard oils directly.

According to Beckurts[2] and Frerichs,[3] on carefully treating chloracetylethylurethane, $ClCH_2CONHCO_2C_2H_5$, with potassium thiocyanate, a mustard oil derivative is formed; namely,

$$SCNCH_2CONHCO_2C_2H_5.$$

The mustard oil structure was assigned to this from the fact that when the compound is treated with alkali and then with hydrochloric acid, hydrogen sulphide is evolved. When this substance is heated it undergoes a molecular rearrangement into what the above authors considered was the normal thiocyanic derivative, but later work showed that the rearranged product was a hydantoïn.[4]

The belief that iso- and normal thiocyanates resulted in this experiment led Frerichs and Beckurts[5] to examine rhodanacetic acid and its derivatives and they claim that none of the salts and esters described by Claësson have the normal form, but that all are derived from isothiocyanic acid. They add that rhodanacetamide prepared from chloracetamide also has the mustard oil structure.

In a later paper, Frerichs and Beckurts[6] state that no normal thiocyanacetic acid exists, and that there are no derivatives of the same. In other words, these compounds are all mustard oils, while according to their last paper[7] rhodanacetanilide has the normal form $NCSCH_2CONHC_6H_5$, and the perfectly analogous rhodanacetmethylanilidehas the iso structure $SCNCH_2CONCH_3C_6H_5$.

The fact that these compounds give off hydrogen sulphide under the above-named conditions is the only fact, as yet published, on which the iso or mustard oil structure is based. Since we have found that certain compounds of the normal form give off hydrogen sulphide under similar treatment, the beautifully crystallizable benzyl thiocyanate, $C_6H_5CH_2SCN$, for example, it is at once evident that this reaction cannot be used as a test for isothiocyanates.

We have, therefore, prepared and examined the behavior of all of

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[1] Hofmann: *Ber. d. chem. Ges.*, **13**, 1350 (1880).

[2] *Arch. d. Pharm.*, **237**, 286.

[3] *Ibid.*, 237, 304 (1899).

[4] *Arch. d. Pharm.*, **238**, 319; *Centrlb.*, **71**, (2), 182 (1900).

[5] *Arch. d. Pharm.*, **238**, 9; *Centrlb.*, **71**, (1), 589 (1900).

[6] *Arch. d. Pharm.*, **238**, 320; *Centrlb.*, **71**, (2), 182 (1900).

[7] *Arch. d. Pharm.*, **238**, 615; *Centrlb.*, **71**, (2), 1270 (1900).

the above compounds as well as various analogues with thiobenzoic acid and our results show conclusively that not a single one of these rhodanides has the mustard oil structure. Not only the esters of Claësson have the formulas originally assigned to them, but also the homologous series of rhodanides, recently prepared in this laboratory, are true thiocyanates.[1]

This is shown by the fact that in the reactions with thiobenzoic acid, the substances combine to form addition products or acyl dithiourethanes. That not even a trace of a mustard oil is present in these compounds follows from the entire absence of carbon disulphide in the reactions.

As far as the authors are aware it has not been observed that the usual molecular rearrangement of thiocyanates into mustard oils is a reversible reaction. Even were this true, in view of the fact that the mustard oils react with thiol acids more readily than with the thiocyanates, the assumption that in these reactions the compounds undergo a rearrangement into normal forms is excluded.

The results, now at hand, show that *neither isothiocyanacetic acid nor any of its derivatives have yet been prepared.*

In Beilstein's Handbuch[2] the rhodanide which results on boiling 1,2-dichlorpropylene with potassium thiocyanate[3] is listed both under the heading of thiocyanates and of mustard oils. We find, when this product is warmed with thiobenzoic acid, that carbon disulphide is evolved in quantity and that 2-chlorpropylene benzamide, $CH_2{=}CCl{-}CH_2NHCOC_6H_6$, is formed. This rhodanide is therefore a mustard oil.

Berthelot[4] states, from thermochemical investigations, that phenyl thiocyanate was observed to be transformed, for the greater part, into isothiocyanate on simply standing during a summer month. Our experiments with this substance do not confirm this statement. We have observed that it remains practically unaltered on keeping at a temperature of 34°–36° for four weeks. Perhaps these conflicting results are to be explained by the fact that, in certain cases, a small amount of foreign substance or impurity acts by catalysis and is capable of producing a molecular rear-

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[1] Wheeler and Barnes: *Am. Chem. J.*, **24**, 60 (1900).

[2] Vol. I, 1279 and 1283.

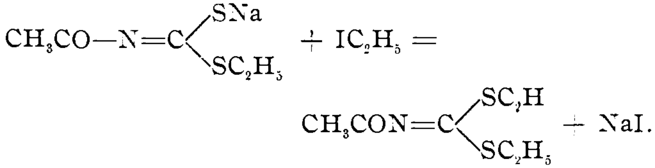
[3] Henry: *Ber. d. chem. Ges.*, **5**, 188 (1872); *Bull. Soc. Chim.*, (Paris), **39**, 526 (1883).

[4] *Compt. rend.*, **132**, 57; *Ann. chim. phys.*, (7), **22**, 327 (1901).

rangement, as in the case of the imido esters and thioncarbamic esters, etc.

The statement of Chanlaroff in regard to the unstable nature of acetyl dithioethylcarbamate would indicate a wide difference between properties of acyl dithiocarbamates and the acyl thioncarbamates ; we find, however, that the two series are closely similar in some respects, and that acylimidodithiocarbonic esters can be obtained from the sodium salts of these carbamates with no greater difficulty than attends the preparation of other imidothiocarbonic esters.[1] The reaction proceeds as follows :

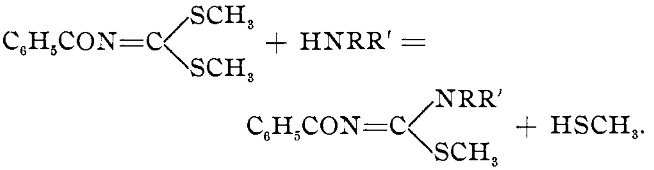
V.



$$CH_3CO{-}N{=}C\left\langle\begin{matrix}SNa\\SC_2H_5\end{matrix}\right. + IC_2H_5 = CH_3CON{=}C\left\langle\begin{matrix}SC_2H\\SC_2H_5\end{matrix}\right. + NaI.$$

The lower members of this series as well as the corresponding benzoyl derivatives distil unaltered under diminished pressure. In a later paper the results of an examination of these compounds will be more fully given, especially those containing different alkyl groups, since, according to Hantzsch, they should exist in stereoisomeric forms. When these acylimidodithiocarbonic esters are treated with ammonia and organic bases a new type of pseudothioureas result. The reaction proceeds smoothly in the cold, with evolution of mercaptan as follows :

VI.



$$C_6H_5CON{=}C\left\langle\begin{matrix}SCH_3\\SCH_3\end{matrix}\right. + HNRR' = C_6H_5CON{=}C\left\langle\begin{matrix}NRR'\\SCH_3\end{matrix}\right. + HSCH_3.$$

Hitherto only one acylpseudothiourea has been obtained in a state of purity,[2] namely, monoacetylethylisodiphenylthiourea, $C_6H_5N = C(SC_2H_5)N(C_6H_5)COCH_3$; this, however, was prepared by a different method. It formed a thick oil which could not be crystallized. The compounds obtained by us differ most decidedly from the oxygen analogues and from the compound of Dains by their great tendency to crystallize and the ease with

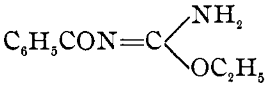
[1] Liebermann : *Ann. Chem.* (Liebig), **207**, 141 (188) ; Fromm and Block : *Ber. d. chem. Ges.*, **32**, 2210 (1899) ; Busch and Lingenbrink : *Ibid.*, 2620 ; Wheeler, Barnes, Johnson, and Dustin : *Am. Chem. J.*, **24**, 60 ; *Ibid.*, 189 ; *Ibid.*, 424 (1900).

[2] Dains : This Journal, **24**, 197 (1900).

which they can be purified. A description of their reactions is reserved for a later paper.

As there appear to be no data in the literature in regard to the behavior of acyldithiocarbamic esters with organic bases we have investigated the action of aniline on some of the acetyl and benzoyl derivatives. It was shown in a previous paper[1] that the acylthioncarbamic esters react in an abnormal manner with ammonia and aniline, that hydrogen sulphide was evolved and pseudoureas were formed. An analogous reaction appears to take place with the dithio esters and aniline ; inasmuch as hydrogen sulphide is evolved, however, by far the chief products are normal ureas, the behavior being more strictly analogous to that of acetylurethane which was thoroughly investigated by Young and Clark.[2] As a contribution to our knowledge of the saponification of urethanes by aniline we examined also the behavior of benzoylethylcarbamate, $C_6H_5CONHCO_2C_2H_5$. We were unable to detect any signs of the formation of a pseudourea in this case; the chief reaction took place with the formation of benzoylphenylurea and alcohol.

As found by Chanlaroff, ammonia acts on the acyldithiocarbamic esters of the above type ; with complete decomposition, mercaptan and ammonium thiocyanate are formed. This reaction is in marked contrast with that of the acylthioncarbamic esters, $C_6H_5CONHCS.OC_2H_5$, for example, which with alcoholic ammonia in the cold, passes quantitatively into benzoylpseudoethylurea,



$$C_6H_5CON{=}C\begin{cases}NH_2\\OC_2H_5\end{cases}$$

In this connection it is interesting to note that the "imidodicarbonsäuretrithiodibenzyl ester," $C_7H_7S.CONHCS.SC_7H_7$, prepared from phenylmethyldithiomonobenzyldi-*c*-methylketuret and concentrated hydrochloric acid, according to Fromm and Junius,[3] reacts in the normal manner since monothiobiuret and benzyl mercaptan are formed. We find that a similar normal reaction takes place with the acylthiolcarbamic esters, mercaptan is evolved, and an acylurea is obtained. These three reactions with ammonia are apparently peculiar to the different series of acyl thiocarbamates.

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[1] *Am. Chem. J.*, **24**, 189 (1900).

[2] *J. Chem. Soc.* (London), **73**, 361 (1898).

[3] *Ber. d. chem. Ges.*, **28**, 1105 (1895).

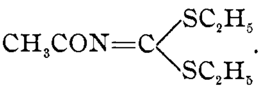
EXPERIMENTAL PART.

The thiocyanates are capable of combining or reacting with thioacetic and thiobenzoic acid at a much lower temperature than that at which Chanlaroff worked. In all cases a smoother reaction is brought about by simply warming a few hours in benzene solution. In certain cases the substances combine at ordinary temperature after long standing. The acyldithiocarbamates thus formed, are all soluble in alkali and most of them can be purified (from disulphide) by precipitating with carbon dioxide. They are converted by a 10 per cent. sodium hydroxide solution, as a rule, into colorless plates of the sodium salts which dissolve on further dilution. The action of alkali, however, produces more or less decomposition into rhodanide and mercaptan, with the formation of thiobenzoic and hydrocyanic salts. They are almost all readily soluble in hot alcohol, but with difficulty in cold, and, like urethanes in general, they form beautiful crystals. They have a yellow color without exception.

Acetyldithiomethyl carbamate, $CH_3CO.NHCS.SCH_3$, is formed practically quantitatively when the constituents are heated dry, or with benzene as a solvent. When crystallized from alcohol it forms long, slender, bright yellow prisms which melt at 119°. A nitrogen determination gave:

	Calculated for $C_4H_7ONS_2$.	Found.
Nitrogen..........	9.3	9.2

Acetyldithioethyl carbamate is the only one of these carbamates that has hitherto been described. It is formed at ordinary temperatures when the rhodanide and thioacetic acid are allowed to stand for a number of weeks, or almost quantitatively when heated for a short time on the water-bath. It forms long, bright yellow prisms which melt at 123°.



Acetyldithiodiethyl carbonate, $CH_3CON{=}C\begin{cases}SC_2H_5\\SC_2H_5\end{cases}$.—When 22 grams of the above carbamate, 3.1 grams of sodium, dissolved in 125 cc. of alcohol, and 20 grams of ethyl bromide were mixed, a reaction took place in a short time and sodium bromide separated. After standing a number of hours, water was added and the precipitated oil was extracted with ether, washed, dried, and distilled at 14 mm. pressure, whereupon 19.2 grams of colorless oil were obtained, boiling sharply at 142° (74 per cent. of the calculated). There was no sign of decomposition during the distillation and an analysis of this oil gave :

	Calculated for $C_7H_{13}ONS_2$.	Found.
Nitrogen..........	7.3	7.6

When this compound is treated with organic bases mercaptan is evolved and pseudothioureas are formed.

Acetyldithionormalpropylcarbamate, $CH_3CONHCS.SC_3H_7$, was prepared from normal propyl rhodanide, boiling at 164° at 761 mm. pressure. This combines smoothly with thioacetic acid and the product crystallizes from dilute alcohol in brilliant yellow plates or flattened prisms melting at 78°. A nitrogen determination gave :

	Calculated for $C_6H_{11}ONS_2$.	Found.
Nitrogen..........	7.9	7.7

Cetyl thiocyanate, $C_{16}H_{32}SCN$.—Kahlbaum's cetyl iodide (30 grams) readily reacted with potassium thiocyanate in alcoholic solution. The product boiled at 242°–249° at 30 mm. pressure, and at 222° to 227° at 13 mm. pressure. It forms a colorless liquid which, on cooling, solidifies to a white wax. The latter portion of the above distillate, when solidified, showed signs of melting at 12° and then melted at 15°–15.5°. A nitrogen determination gave :

	Calculated for $C_{17}H_{33}NS$.	Found.
Nitrogen..........	4.94	4.88

Acetylcetyldithiocarbamate, $CH_3CONHCS.SC_{16}H_{33}$.—The above thiocyanate readily combined with thioacetic acid, on warming three or four hours on the steam-bath. It then solidified to a yellow cake of fine radiating crystals. On crystallizing from alcohol it formed a bulky mass of fine hair-like needles which had a lighter yellow color than the lower members of the series, and which melted at 89°–90°. The material dissolved completely in very dilute alkali ; in moderately dilute, it was converted into a mass of colorless, very thin plates of the sodium salt. An analysis gave :

	Calculated for $C_{19}H_{17}ONS_2$.	Found.
Nitrogen..........	4.13	4.43

Acetyldithiobenzylcarbamate, $CH_3CONHCS.SCH_2C_6H_5$, was smoothly formed from its constituents. It crystallized from alcohol in bright yellow plates melting at 136°, and a nitrogen determination gave :

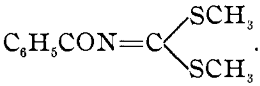
	Calculated for $C_{10}H_{11}ONS_2$.	Found.
Nitrogen..........	6.22	6.50

Benzoyldithiomethylcarbamate, $C_6H_5CONHCS.SCH_3$, is smoothly and apparently quantitatively formed when methyl rhodanide and thiobenzoic acid are warmed for a short time. It forms long, slender, yellow needles melting at 135°, and a nitrogen determination gave :

	Calculated for $C_9H_9ONS_2$.	Found.
Nitrogen..........	6.63	6.34

Benzoyldithioethylcarbamate, $C_6H_5CONHCS.SC_2H_5$, is formed as readily as the methyl derivative. It crystallizes from alcohol in stout, yellow prisms melting at 84°. The determination of nitrogen was as follows :

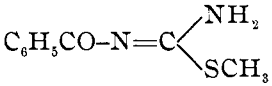
	Calculated for $C_{10}H_{11}ONS_2$.	Found.
Nitrogen..........	6.22	6.22

Benzoyldithiodimethylcarbamate,  $C_6H_5CON{=}C\begin{cases}SCH_3\\SCH_3\end{cases}$.—Twenty grams of benzoyldithiomethylcarbamate were added to a solution of 2.2 grams of sodium, in methyl alcohol, and then 20 grams of methyl iodide. The mixture, on standing a number of hours, was precipitated with water and the product extracted with ether. On evaporating the ether, after drying, long colorless prisms separated which after crystallizing from dilute alcohol melted at 46°. Yield about 15 grams.

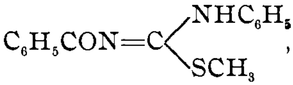
	Calculated for $C_{10}H_{11}ONS_2$.	Found.
Nitrogen..........	6.22	6.26

Benzoyldithiodiethylcarbamate, prepared in a similar manner to the above, proved to be an oil, boiling at 220°–221° at 17 mm. pressure. Ten grams of the urethane gave about 6 grams of the oil, and, on analysis, the following per cent. of nitrogen was obtained :

	Calculated for $C_{12}H_{15}CONS_2$.	Found.
Nitrogen..........	5.53	5.88

Benzoylpseudomethylthiourea,  $C_6H_5CO-N=C{<}^{NH_2}_{SCH_3}$.—When 4.7 grams of benzoyldithiodimethyl carbamate were dissolved in an excess of alcoholic ammonia and allowed to stand for two days, mercaptan separated, and, on evaporating the alcohol and crystallizing the residue from a mixture of benzene and ligroin, about 2 or 3 grams of material melting at 111°–112° were obtained. A nitrogen determination gave:

	Calculated for $C_9H_{10}ON_2S$.	Found.
Nitrogen	14.43	14.53

Benzoylpseudomethylphenylthiourea,  $C_6H_5CON=C{<}^{NHC_6H_5}_{SCH_3}$, was prepared by warming the above dimethyl carbamate, on the water-bath, with aniline. It forms thin colorless plates from alcohol, which melt at 104°–105°.

	Calculated for $C_{15}H_{14}ON_2S$.	Found.
Nitrogen	10.37	10.57

Benzoylpseudoethylphenylthiourea, prepared from the above diethyl carbamate by warming with aniline, formed long colorless prisms from alcohol which melted at 87°–88°.

	Calculated for $C_{16}H_{16}ON_2S$.	Found.
Nitrogen	9.85	9.84

Benzoyldithionormalpropylcarbamate, $C_6H_5CONHCS.SC_3H_7$, is formed as readily as the above dithioethyl carbamate. It crystallizes in bright yellow prisms from alcohol, and it melts at 77°. A nitrogen determination gave:

	Calculated for $C_{11}H_{13}ONS_2$.	Found.
Nitrogen	5.85	5.81

Benzoyldithioisobutylcarbamate, $C_6H_5CONHCS.SC_4H_9$. — This forms transparent golden yellow needles, some over an inch in length, when prepared from isobutylthiocyanate boiling at 178°–180°. It melts at 80°–81°, and an analysis gave:

	Calculated for $C_{12}H_{15}ONS_2$.	Found.
Nitrogen	5.53	5.53

Benzoyldithiocetylcarbamate, $C_6H_5CONHCS.SC_{16}H_{33}$, was formed as smoothly as its lower homologues. It forms a beautiful mass of shining, bright yellow plates, when crystallized from alcohol, and it melts at 63°–64°. A nitrogen determination gave:

	Calculated for $C_{24}H_{39}ONS_2$.	Found.
Nitrogen	3.32	3.30

Benzyl Thiocyanate, $C_6H_5CH_2SCN$.—The melting-point of this compound is given by Henry[1] as 36°–38°, and by Barbaglia[2] as 41°. A portion prepared from benzyl chloride and potassium thiocyanate was crystallized several times from absolute alcohol; it then melted at 43°–43.5°. A portion of this was treated with dilute sodium hydroxide, and on adding acid then, after warming, or on letting the material stand, hydrogen sulphide was given off. This was easily recognized by its odor and the black color it gave with lead acetate paper.

Benzoyldithiobenzylcarbamate, $C_6H_5CONHCS.SCH_2C_6H_5$, results smoothly when the constituents are warmed in benzene solution. No hydrogen cyanide or carbon disulphide is formed in this case. When crystallized from alcohol it forms long yellow needles melting sharply at 108°. A nitrogen determination gave:

	Calculated for $C_{15}H_{13}ONS_2$.	Found.
Nitrogen	4.87	4.92

This compound gives a difficultly soluble sodium salt which separates from aqueous alkali in colorless, thin plates. It is readily soluble in alcohol and it is one of the most stable salts of this series, although warm alkali rapidly decomposes it.

Phenyl Thiocyanate, C_6H_5SCN, *and Thiobenzoic Acid*.—The thiocyanate, in this case, was freshly prepared by the method of Gattermann and Hausknecht.[3] It was allowed to digest, on the water-bath, with thiobenzoic acid for two or three days, whereupon, on cooling, a mass of crystals separated. This material contained no nitrogen and it proved to be identical with *phenyl thiolbenzoate*, $C_6H_5CO.SC_6H_5$, described by Schiller and Otto,[4] and which melts at 56°.

A portion of this thiocyanate (7.8 grams) was allowed to stand at 34°–36° for twenty-eight days, whereupon it was heated with thiobenzoic acid in benzene (20 cc.) for two hours and a

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[1] *Ber. d. chem. Ges.*, **2**, 637 (1869).
[2] *Ibid.*, **5**, 689 (1872).
[3] *Ibid.*, **23**, 739 (1890).
[4] *Ibid.*, **9**, 1635 (1876).

half. The benzene was then distilled off and found to contain some hydrogen cyanide and a small amount of carbon disulphide. On cooling, nothing solid was obtained, and no solid was separated by adding ether (absence of notable quantities of benzanilide). In fact, it was found that a large portion of the rhodanide had remained unaltered in this treatment. Unaltered thiobenzoic acid was removed by alkali, and on evaporating the ether solution, nothing but phenyl thiolbenzoate was obtained. The quantity of benzanilide, if formed at all, was insignificant. These results show that phenyl thiocyanate does not readily undergo a molecular rearrangement into phenyl mustard oil, although Berthelot states, from the results of his thermochemical investigations[1] that the thiocyanate was transformed, for the greater part, on simply standing during a summer month.

2,4-Dinitrophenyl Thiocyanate, $C_6H_3(NO_2)_2SCN$, *and Thioacetic Acid*, when heated together, gave a product insoluble in ether, benzene, and alcohol. From nitrobenzene it crystallized in small yellow pyramids which had no definite melting-point; at 250° it began to decompose and was not completely melted at 280°. It was insoluble in alkali. Although a nitrogen determination agreed with the calculated for a dithiocarbamate, the properties of the substance, however, show that this is *tetranitrophenyldisulphide*, $(C_6H_3(NO_2)_2S—)_2$, which has been described by Willgerodt.[2] The nitrogen determination was as follows:

	Calculated for $(C_6H_3(NO_2)_2S—)_2 = C_{12}H_6O_8N_4S_2$.	Found.
Nitrogen..........	14.0	14.2

When this substance is heated on platinum it explodes.

2,4-Dinitrophenyl Thiocyanate and Thiobenzoic Acid were heated together on the water-bath without benzene. A violent evolution of gas took place which was allowed to pass through water; this then responded to the Prussian-blue test for hydrogen cyanide but gave no test for thiocyanic acid. On crystallizing the residue from 95 per cent. alcohol, plates were obtained which melted at about 100°. This material proved to be impure *benzoyldinitrothiophenol*, which is said to melt at 113° (Willgerodt) or at 111°.[3] On treating this with alkali and then adding acid, the above-mentioned *tetranitrophenyldisulphide* was obtained.

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[1] *Loc. cit.*

[2] Beilstein's "Handbuch," **2**, 816; compare *Ber. d. chem. Ges.*, **9**, 978, and **10**, 1686 (1877).

[3] Kym: *Ber. d. chem. Ges.*, **32**, 3532 (1899).

Rhodanacetylethylurethane and Thiobenzoic Acid.—If rhodanacetylethylurethane has a mustard oil structure it should act with thiobenzoic acid with the formation of hippurylurethane and carbon disulphide. Instead of this, the action took an entirely different course. 5.7 grams of the rhodanide, prepared according to the directions of Frerichs, and melting at 86°, were dissolved in 45 cc. of benzene, and 4.2 grams of thiobenzoic acid were added. The mixture was heated on the water-bath for eight hours, with a return condenser, whereupon a portion of the benzene was distilled off and tested for carbon disulphide, by adding an alcoholic solution of potassium hydroxide. No precipitate of potassium xanthate was obtained, and on adding copper sulphate solution no yellow precipitate resulted. The reaction product was therefore free from carbon disulphide. The alkaline solution gave the Prussian blue test for hydrogen cyanide. The benzene solution was filtered from a small amount of material and, on cooling, minute yellow crystals separated. These formed the chief product of the reaction. When these were crystallized from alcohol thin, golden yellow plates were obtained, which melted at 159°. The color and the following analysis show that this substance is *benzoyldithiocarbamicacetylethylurethane*,

$$C_6H_5CONHCS.SCH_2CONHCO_2C_2H_5:$$

	Calculated for $C_{13}H_{14}O_4N_2S_2$.	Found.
Nitrogen	8.58	8.50

Rhodanacetylethylurethane, therefore, has the structure

$$NCS.CH_2CONHCO_2C_2H_5.$$

Rhodanmethyl Acetate and Thiobenzoic Acid.—The action of the thiocyanic esters of acetic acid with thiol acids is well represented by rhodanmethyl acetate. The behavior of this alone is described here since that of others as well as certain homologues have been used in other work and will be described in a later paper. When the rhodanide in question was warmed with thiobenzoic acid no carbon disulphide resulted and no methyl hippurate was obtained. Thirteen grams of thiobenzoic acid and 12 grams of rhodanmethyl acetate were diluted with 30 cc. of benzene and heated to boiling for six hours. On evaporating off the benzene and crystallizing from alcohol, 14 grams of bright yellow prisms melting at 118° were easily obtained. The properties of the substance and the following nitrogen determination show that this is *benzoyldithiocarbamicmethyl acetate*, $C_6H_5CONHCS.SCH_2CO_2CH_3$:

	Calculated for $C_{11}H_{11}O_3NS_2$.	Found.
Nitrogen..........	5.24	5.65

In the process of formation of the above, traces of hydrogen cyanide are evolved, but otherwise, there appears to be very little by-products formed. It follows, therefore, that rhodanmethyl acetate is a derivative of normal thiocyanic acid and not a mustard oil.

Rhodanacetamide and Thiobenzoic acid, on heating together in benzene solution, evolved hydrogen cyanide and on cooling benzoyldisulphide separated in quantity. On distilling off the benzene and testing for carbon disulphide none was found. This fact establishes that rhodanacetamide is not a mustard oil. The remaining material in the benzene solution was not obtained in a state of purity. It formed a black tar.

Benzoylthioglycollamide, $C_6H_5COSCH_2CONH_2$.—This was prepared from potassium thiolbenzoate and chloracetamide, in order to compare it with the products in the above experiment. It crystallizes from hot water in long colorless prisms which melt at 119°–120°. A nitrogen determination gave:

	Calculated for $C_9H_9O_2NS$.	Found.
Nitrogen..........	7.18	7.35

Rhodanacetmethylanilide and Thiobenzoic Acid.—When 6.6 grams of this rhodanide and 4.4 grams of thiobenzoic acid with 35 cc. benzene were heated for five hours on the water-bath, no carbon disulphide was formed and nothing corresponding to hippurmethylanilide was obtained. The Prussian blue test showed the presence of hydrogen cyanide and on evaporating off the benzene a tar was found. On treating this with ether and on crystallizing the solid which separated from dilute alcohol yellow, flattened prisms or tables were obtained, which melted at 152° (0.2–0.3 gram). A nitrogen determination agreed with the calculated for *benzoyldithiocarbamicmethylacetanilide*,

$$C_6H_5CONHCS.SCH_2CON(CH_3)C_6H_5 :$$

	Calculated for $C_{17}H_{16}O_2N_2S_2$.	Found.
Nitrogen..........	8.13	8.08

The above results show that rhodanacetmethylanilide is a derivative of normal and not isothiocyanic acid.

Allyl Isothiocyanate, C_3H_5NCS, *and Thiobenzoic Acid* react immediately on gently warming, carbon disulphide streams off and the remaining light yellow colored oil distils almost entirely from 175°–176° at 14 mm. pressure. Kay[1] gives the boiling-point of *allyl-benzamide* as 173°–174° at 14 mm. pressure. The carbon disulphide evolved in these reactions is pure and it has no disagreeable odor, but suggests somewhat that of ether. That it is carbon disulphide was shown in each case by the xanthate test.

Phenyl Isothiocyanate, C_6H_5NCS, *and Thiobenzoic Acid* reacted very readily on the steam-bath; carbon disulphide was evolved and the residue solidified. On crystallizing from alcohol large plates of *benzanilide* melting at 161° were obtained.

Phenyl Isothiocyanate and Thioacetic Acid on standing at ordinary temperatures for a month deposited a mass of colorless plates of acetanilide melting at 114°.

α-Chlorallyl Isothiocyanate, $CH_2{=}CCl{-}CH_2NCS$, *and Thiobenzoic Acid.*—The isothiocyanate was prepared according to the directions of Henry and 5 grams of this were heated with 5.2 grams of thiobenzoic acid in 45 cc. of benzene. After six hours a portion of the benzene was distilled off and this gave an abundant precipitate of xanthate with alcoholic potassium hydroxide. No hydrogen cyanide could be detected. The reaction product was boiled with water to remove some oil and then crystallized from a mixture of benzene and petroleum ether whereupon it was obtained in long colorless flattened prisms melting at 95°. A nitrogen determination agreed with the calculated for *2-chlorallyl-benzamide*, $C_6H_5CONHCH_2{-}CCl{=}CH_2$:

	Calculated for $C_{10}H_{10}NCl$.	Found.
Nitrogen	7.17	7.31

Benzoyl Rhodanide, C_6H_5CONCS, *and Thiobenzoic Acid* were warmed for a short time on the water-bath, carbon disulphide was given off, and the residue was treated with alkali and ether (to remove some benzonitrile). The alkaline solution on acidifying gave a product which, on crystallizing from dilute alcohol, formed needles melting at 148°. This material was, therefore, *dibenzamide*.

[1] *Loc. cit.*

Ethyl Selenocyanide, C_2H_5SeCN.—This compound, which appears to be new, was prepared from 16.1 grams of potassium selenocyanide and 15 grams of ethyl bromide in alcohol solution. The reaction is complete in a few minutes, and it is best then to add water without distilling off the alcohol. The oil is somewhat volatile in alcohol vapor and also in that of ether. On distilling at 741 mm. pressure it practically all boiled at 172°. It formed a pale yellow oil with a highly disagreeable odor. A nitrogen determination gave :

	Calculated for C_3H_5NSe.	Found.
Nitrogen	10.44	10.38

When this was warmed with thiobenzoic acid it gave off a gas or vapor, with the odor of hydrogen cyanide, and an oil and a solid were obtained. These products were not investigated.

AN IMPROVED METHOD FOR THE RAPID ESTIMATION OF SUGAR IN BEETS.

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INTRODUCTION.

EXPERIENCE has abundantly shown that both the good and the bad properties of any individual beet are largely hereditary and may be transmitted to succeeding generations of beets. The success of the beet-sugar industry in recent times has been due to a very large extent to the building up of a race of high-grade beets by means of the selection of individual beets having high sugar content for the production of the seed for later use. Long-continued and careful efforts in this direction have resulted in the production of beets of highly satisfactory sugar-producing qualities. This condition is more or less abnormal, however, and the tendency is toward a retrogression or reversion to the original state. In order to prevent this and to maintain the present high state of perfection, constant care in the selection of only the best beets for mothers for seed production is necessary. Not only is it essential to select those beets which possess the best form of leaves and root, but care must also be taken that only those whose roots are of high sugar content are used. The sugar content of individual beet roots under the same conditions of growth varies