acids in alcohol, with the conductivities of these same compounds in water, reference must be had to *Publication of the Carnegie Institution of Washington*, No. 170 (1912).

BALTIMORE, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS.]

ON THE ACTION OF CERTAIN ACID REAGENTS ON THE SUBSTITUTED UREAS AND THIAZOLE.

[SECOND PAPER.]

BY F. B. DAINS, R. C. ROBERTS AND R. Q. BREWSTER.

This is a continuation of an investigation[1] begun several years ago on the reactivity of the anilido hydrogen in the oxygen and sulfur ureas and is a study of the effect of acyl reagents on the grouping —NHCO(S)NH— or NH — C = NR in both open-chain and ring-compounds.

$$\text{SR}$$

Disubstituted Ureas and Acid Chlorides.—As has been previously shown, a urea of the type RNHCONHR reacts with an acid chloride at 150–160° giving the amidine hydrochloride, RNH — C = NR, HCl and

$$R$$

carbon dioxide. An acyl derivative of the urea is first formed. This then dissociates into carbanilide and an isocyanate, RNHCOR + RNCO, which at the temperature employed react giving carbon dioxide and the amidine.[2]

Molecular proportions of benzoyl chloride and di-*o*-tolylurea were heated in a sealed tube at 170° for four hours. The tube opened with pressure, due to carbon dioxide and hydrogen chloride, while the odor of isocyanate could be detected in the escaping gases. The solid contents of the tube consisted of benz-*o*-toluide and the hydrogen chloride salt of a base, which was freely soluble in water. The base, benz-di-*o*-tolyl-amidine, $C_6H_5 — C = NC_7H_7(NHC_7H_7)$ was precipitated with sodium hydroxide and purified by crystallization from alcohol, in which it is easily soluble. It separated in fine, white needles melting at 87–8°.

Calc. for $C_{21}H_{20}N_2$: N, 9.33%. Found: 9.44%.

Diphenylurea and isovaleryl chloride react at 140° giving a base, isovaler-diphenylamidine, which melts at 103°. It was identified by the analysis of the yellow platinum salt, which has a melting point of 207°.

Calc. for $(C_{17}H_{20}N_2)_2H_2PtCl_6$: Pt, 21.35%. Found: 21.22%, 21.44%.

[1] THIS JOURNAL, **22**, 181 (1900).

[2] *Ibid.*, **22**, 188 (1900).

The picrate of this base melts at 144–5°. This is possibly identical with the amidine obtained by Hofmann[1] as a result of heating isovaleric acid, anilin and phosphorus trichloride. His product melted at 111°.

Di-m-tolylurea and isovaleryl chloride were heated in a sealed tube at 140–50°. From the reaction product was isolated the base, isovaler-di-m-tolylamidine, which crystallizes in fine, white needles melting at 102°.

Calc. for $C_{19}H_{24}N_2$: N, 10.00%. Found: 10.64%.

The yellow platinum salt melts at 214°.

Calc. for $(C_{19}H_{24}N_2)_2H_2PtCl_6$: Pt, 20.01%. Found: 20.09%.

From di-p-tolylurea and isovaleryl chloride was obtained isovaler-di-p-tolylamidine, white crystals from alcohol with a melting point of 91–2°.

Calc. for $C_{19}H_{24}N_2$: N, 10.00%. Found: 9.86%.

The amidine hydrochloride melts at 175° and the platinum salt at 199°.

Calc. for $(C_{19}H_{24}N_2)_2H_2PtCl_6$: Pt, 20.01%. Found: 20.19%.

Under like conditions, molar proportions of di-p-tolylurea and m-nitrobenzoyl chloride gave m-nitrobenz-p-toluide and the base m-nitrobenz-di-p-tolylamidine. This separates from alcohol in fine, yellow needles, which melt at 137°.

Calc. for $C_{21}H_{19}O_2N_3$: N, 12.18%. Found: 12.27%.

Thioureas and Acid Chlorides.—Previous investigations have shown[2] that the substituted thioureas and acid chlorides may react with the formation of an acyl derivative of the urea, a molecular addition product of the urea and the acid chloride, or at an elevated temperature with the production of a mustard oil and a substituted acid amide. Additional evidence is afforded by the following experiments: Thus at 90°, acetyl chloride and di-α-naphthylthiourea give α-naphthyl mustard oil and α-acetnaphthalide, while at 160° the same urea reacts with benzoyl chloride with the formation of the mustard oil and α-benznaphthalide. Only traces of a basic product are formed.

Corresponding results are obtained when a diacid chloride is used. When a molar mixture of thiocarbanilide and phthalyl chloride is heated at 160°, the main products are phenyl mustard oil and phthalanil in accordance with the following equation:

$$C_6H_4(COCl)_2 + C_6H_5NHCSNHC_6H_5 =$$
$$C_6H_5NCS + C_6H_4(CO)_2NC_6H_5 + 2HCl$$
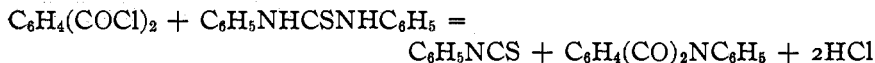
A small amount of triphenylguanidine is also formed, as a result probably of the action of hydrogen chloride on the thiocarbanilide.

Under like conditions, phthalyl chloride and diphenyl urea give chiefly phthalanil, although the odor of phenyl isocyanate as well as phosgene

[1] Hofmann, *Jahresb.*, **1865**, 416.

[2] Deninger, *Ber.*, **28**, 1332 (1895); Dixon, *J. Chem. Soc.*, **101**, 2522 (1912); Dains, THIS JOURNAL, **22**, 191 (1900).

was noted on opening the tube. It would seem that at 160° the iso-cyanate was capable of reacting with the acid chloride giving phthalanil and carbonyl chloride.

$$C_6H_4(COCl)_2 + C_6H_5NCO = C_6H_4(CO)_2NC_6H_5 + COCl_2.$$

No amidine formation occurs as in the case of the simple acid chloride.

Thioureas and Urea Chlorides.—Dixon[1] found that when thiocarbanilide was heated with methyl phenyl urea chloride, there resulted phenyl mustard oil and triphenyl guanidine. Some years ago, before Dixon's work appeared, the action of diphenyl urea chloride on certain thioureas was tried, and as the results confirm the investigation of Dixon, they will be briefly noted. Thiocarbanilide and diphenyl urea chloride react easily and smoothly at 110–120° with the formation of carbonyl sulfide, phenyl mustard oil, triphenyl guanidine and diphenylamine, according to the general equation

$$(C_6H_5)_2NCOCl + 2RNHCSNHR =$$
$$(C_6H_5)_2NH + COS + RNCS + (RNH)_2C = NR.HCl.$$
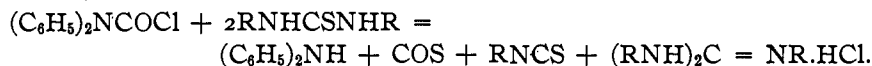
Under like conditions, the urea chloride and di-p-tolylthiourea gave p-tolyl mustard oil and tri-p-tolyl guanidine, while from di-o-tolylthio-urea was isolated the corresponding mustard oil and guanidine. The guanidines were identified by their melting points and the analysis of their platinum salts.

That the oxygen ureas behave in a similar manner was shown by the fact that when diphenylurea and diphenylurea chloride were heated at 170° in a sealed tube, the products were carbon dioxide, phenyl isocyanate and triphenyl guanidine.

The trisubstituted thioureas, compounds of the type $R_2NCSNHR$, contain an anilido hydrogen which can be easily replaced by an acyl group. Thus Dixon and Taylor[2] have shown that α,β-diphenyl-α-methylthiourea and benzoyl chloride form an addition product, which readily loses hydrogen chloride yielding benzoyl-diphenyl-methyl-thio-urea, a stable compound not easily desulfurized.

The same ease of replacement was noticed in the case of diphenyl-ethyl-thiourea and carbonyl chloride. To a benzene solution of the thiourea (two mols) and pyridine (two mols) was added a molar solution of phosgene in benzene. The solution became warm and pyridine hydro-chloride was deposited. From the benzene solution was isolated a com-pound, which crystallizes from alcohol in fine, white needles, melting at 166°. The analysis gave figures corresponding to carbonyl bis-diphenyl-ethyl-thiourea, $CO(NC_6H_5CSNC_6H_5.C_2H_5)_2$.

Calc. for $C_{31}H_{30}ON_4S$: N, 10.41%. Found: 10.62%, 10.50%.

[1] *J. Chem. Soc.*, **75**, 405 (1899).
[2] *Ibid.*, **101**, 2522 (1912).

It is not desulfurized by boiling with mercuric oxide in benzene solution.

Urea Chlorides and Tri-substituted Thioureas. Synthesis of Tetra-substituted Oxygen Ureas.—Efforts to bring about reaction between the trisubstituted thioureas and urea chloride in solution, even in the presence of pyridine, have thus far proved fruitless. Dixon[1] met with the same success, as he found that benzyl-phenyl-ethyl-thiourea was not affected by diphenyl urea chloride in a boiling chloroform solution.

However, when higher temperatures are used the following general reaction occurs, giving a mustard oil and a tetra-substituted urea:

$$R_2NCSNHR + ClCONR_2 = HCl + RNCS + R_2NCONR_2$$
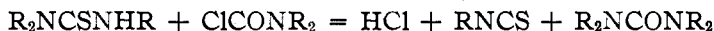
Molar quantities of diphenyl-methyl-thiourea and diphenyl urea chloride were heated in an oil bath at 150°. From the reaction product was obtained phenyl mustard oil and a sulfur free compound melting at 105°. It was readily soluble in alcohol and proved to be triphenyl-methyl-urea, $(C_6H_5)_2NCONC_6H_5.CH_3$.

Calc. for $C_{20}H_{18}ON_2$: 9.27%. Found: 9.44%, 9.45%.

Under like conditions, diphenyl-methyl-thiourea and phenyl methyl urea chloride gave phenyl mustard oil and diphenyl-dimethyl-urea, identical with the product obtained by Michler and Zimmermann.[2]

From diphenyl-ethyl-thiourea and diphenyl urea chloride was obtained the phenyl mustard oil and triphenyl-ethyl urea (m. p. 79°).[3]

Equal mols of diphenyl-ethyl-thiourea and phenyl methyl urea chloride react at 150–60° yielding the mustard oil and α,β-diphenyl-α,β-methyl-ethyl urea. It was purified by crystallization from gasoline and is easily soluble in alcohol and benzene, sparingly so in ether. It melts at 74°.

Calc. for $C_{16}H_{18}O_2N$: 11.02%. Found: 11.15%, 11.35%.

The same urea was prepared and its constitution thus proven, by heating a mixture of phenyl-ethyl-amine, phenyl methyl urea chloride and pyridine at 140°.

Isothiourea Ethers and Acid Chlorides.—In a previous paper,[4] results were obtained which indicated that the anilido hydrogen of isothiourea ethers of the type, $RN = C(NHR)SR$, could be easily replaced by an acyl group. The following experimental work substantiates this view. The methyl ether of isothiodiphenyl urea was heated at water bath temperature for fifteen minutes with a little more than one equivalent of acetic anhydride, the resulting light yellow liquid was dissolved in alcohol, diluted with water and allowed to stand and the white solid which gradually precipitated re-dissolved in hot dilute alcohol from which it separated

[1] *J. Chem. Soc.*, **75**, 399 (1899).

[2] *Ber.*, **12**, 1166 (1879); *Jahrb.*, **1881**, 335.

[3] *Ber.*, **9**, 712 (1876); **14**, 2185 (1881).

[4] THIS JOURNAL, **22**, 196 (1900).

in cubical crystals melting at 71°. It proved to be the methyl ether of acetyl-isothiodiphenyl urea, $C_6H_5N = C - N(COCH_3)C_6H_5$.

$$| \\ SCH_3$$

Calc. for $C_{16}H_{16}ON_2S$: N, 9.78%. Found: 9.90%, 10.04%.

The addition of the acetyl group has greatly reduced the basic properties of the isothiourea ether. The acyl derivative is only slightly soluble in dilute acids. It does not form a solid hydrochloride, when hydrogen chloride is passed into its benzene solution, nor does it give a picrate. Alkalies split off the acetyl group giving the original ether. It is more stable, however, than the corresponding acetyl derivative of the simple thiocarbanilide, since that dissociates above its melting point into mustard oil and acetanilide.

Methyl acetyl-isothiodiphenyl urea is readily soluble in chloroform, benzene and gasoline, but only moderately so in ether.

The same acetyl derivative can be easily prepared by adding acetyl chloride (one mol) to a benzene solution of the methyl ether (two mols) and allowing the mixture to stand. On examination the supernatant liquid was found to contain the acetyl compound, while the solid residue consisted of the hydrogen chloride salt of the original methyl isothiourea ether.

The Ethyl Ether of *m*-Nitrobenzoyl Isothio-di-*o*-tolyl-urea, $C_7H_7N : C - S - C_2H_5$

$$| \\ C_7H_7 - N - COC_6H_4NO_2$$

.—Molecular quantities of the ethyl ether and pyridine (to unite with the hydrogen chloride) were dissolved in benzene and the *m*-nitro-benzoyl chloride slowly added. After filtering from the pyridine hydrochloride, the evaporation of the benzene solution gave the nitro-benzoyl derivative, which after recrystallization melted at 122°.

Calc. for $C_{24}H_{23}O_3N_3S$: N, 9.70%. Found: 9.85%, 9.90%.

The compound is not basic and is readily decomposed by boiling alcoholic potash, giving ethyl mercaptan, di-*o*-tolyl urea and *m*-nitrobenzoic acid.

Under like conditions the methyl ether of isothiodiphenyl urea, pyridine and *m*-nitro-benzoyl chloride gave the methyl ether of *m*-nitrobenzoyl-isothio-diphenyl urea. Purified from gasoline, it melts at 101°

Calc. for $C_{21}H_{17}O_3N_3S$: N, 10.70%. Found: 10.51%, 10.60%.

The Isothiourea Ethers and Urea Chlorides.—From the ease of substitution of an acyl group in the isoureaethers and the general stability of the molecule, it was thought that there might be a possibility of introducing the grouping R_2NCO in place of the anilido hydrogen in these compounds. All efforts to bring about combination at the temperature of boiling benzene were without success, while at higher temperatures the

following reaction was found to occur with the formation of an alkyl chloride, mustard oils and a trisubstituted urea.

$$RNHC - SR + R_2NCOCl = RNCS + RCl + RNHCONR_2.$$
$$\quad \| $$
$$\quad NR$$
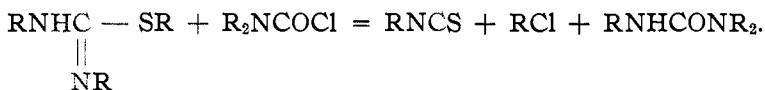
The methyl ether of isothio-diphenyl urea and diphenyl urea chloride were heated in a sealed tube at 150° for four hours. The tube opened with pressure, due to methyl chloride and the odor of mercaptan was noticeable. From the contents of the tube were isolated phenyl mustard oil and methyl-diphenyl urea, white crystals from gasoline, melting at 106°.

<div align="center">Calc. for $C_{14}H_{14}ON_2$: N, 12.41%. Found: 12.63%.</div>

It was further identified by its synthesis from aniline and methyl phenyl urea chloride. The same urea was obtained by Gebhardt[1] from phenyl isocyanate and mono-methyl analine.

o-**Tolyl-methyl-phenyl Urea.**—The ethyl ether of isothio-*o*-tolyl urea and methyl phenyl urea chloride were heated at 150° with the resulting formation of ethyl chloride, *o*-tolyl mustard oil and *o*-tolyl methyl phenyl urea, $C_7H_7NHCON(CH_3)C_6H_5$. This crystallized from gasoline in fine, white needles melting at 117°. The same urea was also prepared by heating *o*-toluidine and the methyl phenyl urea chloride at 125°.

<div align="center">Calc. for $C_{15}H_{16}ON_2$: N, 11.66%. Found: 11.50%, 11.72%.</div>

Under like conditions, diphenyl urea chloride and the ethyl ether of isothio di-*o*-tolyl urea gave ethyl chloride, *o*-tolyl mustard oil and α,α-di-phenyl-β-*o*-tolyl urea, white crystals easily soluble in alcohol, benzene and chloroform, moderately soluble in gasoline, with a melting point of 85°.

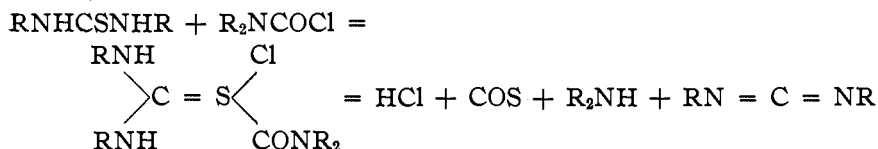<div align="center">Calc. for $C_{20}H_{18}ON_2$: N, 9.27%. Found: 9.05%, 9.11%.</div>

The mechanism of the reaction between the urea chlorides and the substituted ureas and the thiourea ethers is open to question. Dixon[2] has suggested that the acyl chlorides react by first addition to the sulfur atom which becomes tetravalent. These addition products which have been isolated in many cases break down, either by heating above their dissociation points or under the influence of solvents, loss of halogen hydride occurs and the acid group of the type RCO migrates to a nitrogen, giving acyl nitrogen derivatives. The stability of the resulting sub-stitution product seems to depend upon the presence of a reactive anilido hydrogen. Thus acetyl-diphenyl thiourea easily dissociates into acet-anilide and phenyl mustard oil, while the dibenzoyl diphenyl thiourea is stable. When a phenyl group is replaced by the more positive allyl grouping the ease of decomposition seems to be increased, as will be
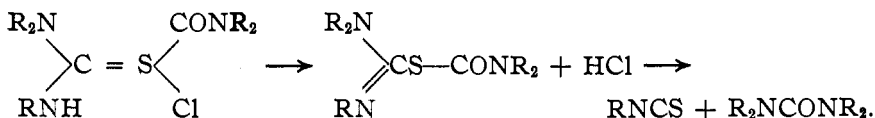
1 *Ber.*, **17**, 2593 (1884).
2 *J. Chem. Soc.*, **101**, 2519 (1912).

noted later.   This assumption of first addition to the sulfur atom affords a logical explanation of the action of the urea chlorides.   For instance, diphenyl-thiourea and a urea chloride could react as follows:

RNHCSNHR + R$_2$NCOCl =

$$\begin{array}{cc} \text{RNH} & \text{Cl} \\ \diagdown & \diagup \\ \text{C} = \text{S} & = \text{HCl} + \text{COS} + \text{R}_2\text{NH} + \text{RN} = \text{C} = \text{NR} \\ \diagup & \diagdown \\ \text{RNH} & \text{CONR}_2 \end{array}$$
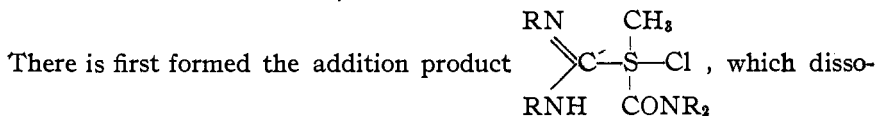
The addition compound breaks down into the simpler products hydrogen chloride, carbonyl sulfide, diphenylamine and carbodiimide.

The carbodiimide now attacks a mol of unchanged thiourea, yielding triphenyl-guanidine and phenyl mustard oil.   The explanation agrees wholly with experimental facts.   In the case of the trisubstituted thioureas the first addition product would be

$$\begin{array}{cccc} \text{R}_2\text{N} & \text{CONR}_2 & \text{R}_2\text{N} \\ \diagdown & \diagup & \diagdown \\ \text{C} = \text{S} & \longrightarrow & \text{CS—CONR}_2 + \text{HCl} \longrightarrow \\ \diagup & \diagdown & \diagup \\ \text{RNH} & \text{Cl} & \text{RN} & \text{RNCS} + \text{R}_2\text{NCONR}_2. \end{array}$$

Here the absence of hydrogen prevents the formation of diphenylamine and the compounds breaks down into the mustard oil and a tetrasubstituted urea.

With the thiourea ethers, the reaction can be formulated as follows:

$$\begin{array}{cc} \text{RN} & \text{CH}_3 \\ \diagdown & | \\ \text{There is first formed the addition product} \quad \text{C—S—Cl} \, , \text{ which disso-} \\ \diagup & | \\ \text{RNH} & \text{CONR}_2 \end{array}$$

ciated into methyl chloride, mustard oil and a trisubstituted oxygen urea.

Allyl Thioureas and Acid Chlorides.—In a previous paper,[1] it was shown that acetyl chloride acting directly without a solvent upon allyl-phenyl-thiourea converted it easily and smoothly into the isomeric 2-anilido-5-'methyl-4,5-dihydrothiazole.   Dixon later made the same observation.[2] We have now found that by modifying the conditions, it is possible to obtain from the allyl thioureas and acyl chlorides, not only the thiazoles but also their acyl derivatives.   Molar proportions of allyl-phenyl-thiourea and pyridine were dissolved in benzene and one mol of benzoyl chloride added to the mixture.   After standing, the benzene solution was filtered from the pyridine hydrochloride and the solution washed with dilute acid to remove any excess pyridine.   From the benzene on evaporation at room temperature white crystals melting at 125° were obtained, which proved to be α-allyl-β,β-benzoyl-phenylthiourea, C$_3$H$_5$NHCS-(COC$_6$H$_5$)C$_6$H$_5$.   That the above constitution is correct is shown by the

[1] THIS JOURNAL, **22**, 192 (1900).
[2] *J. Chem. Soc.*, **93**, 24 (1908).

fact that when the benzene solution of the allyl-benzoyl-phenyl thiourea. is concentrated with the aid of heat, it decomposes quantitatively into allyl mustard oil and benzanilide.

Acetyl chloride was allowed to react with a mixture of allyl phenyl thiourea and pyridine in benzene solution. After removal of the pyridine and pyridine hydrochloride, the solution was allowed to evaporate at room temperature. The only products obtained were allyl mustard oil and acetanilide. The acetyl-phenyl allyl thiourea, which must have been first formed, evidently breaks down with very great ease. With a substituted phenyl group, the acetyl derivative. is more stable. Thus. acetyl chloride was added to a benzene solution of allyl p-bromophenyl thiourea. From the benzene solution was obtained by evaporation the allyl-acetyl-p-bromo-phenyl thiourea. This separates in white crystals. melting at 86°.

<div align="center">Calc. for $C_{12}H_{13}ON_2BrS$: Br, 24.42%. Found: 24.11%.</div>

Alcoholic potash removes the acetyl group giving the original thiourea. Warming the compound above its melting point for a few minutes causes it to break down into allyl mustard oil and p-bromo-acetanilide.

Under similar conditions, acetyl chloride and allyl-p-chloro-phenyl-thiourea gave α-allyl-β-acetyl-β-p-chloro-phenyl thiourea, white crystals. from benzene melting at 84°.

<div align="center">Calc. for $C_{12}H_{13}ON_2ClS$: Cl, 13.50%. Found: 13.21%.</div>

Heated above its melting point, it decomposed into allyl mustard oil and impure p-chloro-acetanilide.

It will be noted in the case of these allyl phenyl thioureas, that the acyl group attaches itself to the nitrogen of the more negative anilido rest and not to the more positive C_3H_5N grouping.

This would seem to be in accord with some previous experimental work,[1] where it was found that when an acid chloride was added to a mixture of two different amines, there was formed the hydrochloride of the more positive amine and the acyl derivative of the more negative one. Whether this will hold good in all cases with thioureas of the type R'NHCSNHR must await further investigation.

Allyl Thioureas and Acid Chlorides. Thiazole Synthesis.—It has been mentioned before that allyl phenyl thiourea with acetyl chloride, in the absence of a solvent, rearrranged to a thiazole derivative. The same result is attained when the thiourea and benzoyl chloride are heated at water bath temperature for thirty minutes.

2-p-Bromophenylamido-5-methyl-4,5-dihydrothiazol.—This is easily made by heating p-bromo-phenyl allyl thiourea with acetyl chloride for twenty minutes. The reaction product was dissolved in dilute alcohol

[1] Dains, THIS JOURNAL, 28, 1184 (1906).

and then made alkaline with sodium carbonate solution. The white precipitate after recrystallization from alcohol melted at 107°. It is soluble in the ordinary organic solvents and in acids. Its picrate melts at 156°. The same thiazole was prepared by heating the allyl-p-bromo-phenyl-thiourea and concentrated hydrochloric acid in a pressure flask on the water bath until all the thiourea had gone into solution.

<div style="text-align:center">Calc. for $C_{10}H_{11}N_2BrS$: N, 10.40%. Found: 10.70%, 10.63%.</div>

2-p-Chloro-phenylamido-5-methyl-4,5-dihydro-thiazole   from   acetyl chloride and allyl p-chloro-phenyl thiourea forms white crystals out of alcohol, melting at 116°.

<div style="text-align:center">Calc. for $C_{10}H_{11}N_2ClS$: N, 12.40%. Found: 12.58%.</div>
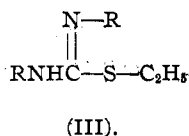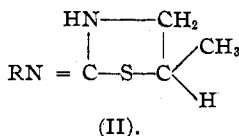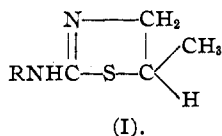
Its hydrochloric acid salt is precipitated when dry hydrogen chloride is passed into the benzene solution of the base. It melts at 226°

<div style="text-align:center">Calc. for $C_{10}H_{11}N_2ClS.HCl$: HCl, 13.86%. Found: 14.20%.</div>

m-Tolylamido-5-methyl-4,5-dihydrothiazol.—Acetyl chloride converts the allyl-m-tolyl-thiourea quantitatively into the corresponding thiazole. This recrystallized from alcohol melts at 90°. The picrate melts at 158°. It is readily soluble in alcohol, benzene, gasoline and dilute acids, very soluble in chloroform.
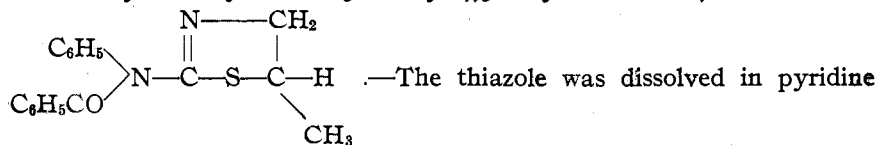
<div style="text-align:center">Calc. for $C_{11}H_{14}N_2S$: N, 13.60%. Found: 13.48%, 13.26%.</div>

The Thiazoles and Acid Chloride.—It will be noticed that the thiazoles thus formed bear a close relationship in structure to the isothiourea ethers. Both types of compounds contain an amidine grouping and a sulfur atom linked to two carbons.

<div style="text-align:center">
N——CH₂   HN——CH₂   N—R
‖ | /CH₃ | | /CH₃   ‖
RNHC—S—C<   RN = C—S—C<   RNHC—S—C₂H₅
       \H   \H
(I).   (II).   (III).
</div>

Formulas I and II show the tautomeric forms of the same thiazole and III an isothiourea ether with analogous grouping. The anilido hydrogen in the isourea ethers can be easily replaced by an acyl group, and experiment has shown that the corresponding hydrogen in the thiazoles is equally reactive toward acetic anhydride,[1]

2-Phenyl-benzoyl-amido-5-methyl-4,5-dihydro-thiazole,

<div style="text-align:center">
N——CH₂
C₆H₅\   ‖ |
    >N—C—S—C—H   —The thiazole was dissolved in pyridine
C₆H₅CO/   \
             CH₃
</div>

and benzoyl chloride added. From the reaction product was isolated

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[1] Young and Crookes, *J. Chem. Soc.*, **89**, 65 (1906); Traumann, *Ann.*, **244**, 31 (1888).

the above benzoyl derivative. Purified from alcohol it separates in white crystals melting at 118°. It is soluble in ether, readily soluble in carbon bisulfide, alcohol and benzene, very soluble in chloroform.

<div align="center">Calc. for $C_{17}H_{16}ON_2S$: N, 9.46%. Found: 9.65%, 9.74%.</div>

It is isomeric with the allyl-phenyl-benzoyl-thiourea. The thiazole is no longer basic and the benzoyl group is easily split off by either alcoholic potash or cold hydrochloric acid, yielding the original thiazole. There is of course a possibility that the benzoyl group is attached to the nitrogen at 2, but the evidence seems to be in favor of the above formula. Thus Prager[1] and Young and Crookes[2] have shown that when this thiazole unites with methyl iodide, the methyl group goes to the nitrogen to which the phenyl group is attached and secondly it has been pointed out in this paper that when benzoyl chloride acts on allyl-phenyl-thiourea, the product contains a benzoyl and a phenyl group on the same nitrogen atom.

Further investigation along these lines is being continued in this laboratory.

LAWRENCE, KANSAS.

RESEARCHES ON ORGANIC PERIODIDES.
I. PERIODIDES OF PHENACETIN, METHACETIN AND TRIPHENIN.

By W. O. EMERY.

Introduction.

The first comprehensive study of organic periodides was inaugurated by Joergensen[3] in 1869. Since that time many new periodides as well as other perhalides of both organic and inorganic bases have been prepared and investigated more or less thoroughly from varying viewpoints, notably as regards composition, mechanism of formation and availability for purposes of quantitative analysis.

In connection with a general plan for the systematic development of tests and methods applicable to drug analysis, it was decided to investigate the iodine addition-products or periodides of some of the more important synthetic compounds of a quasi-alkaloidal character, with a view to the eventual use of such products in analytical operations.

The study of periodides in general, as also those of the phenetidine type in particular, had its inception in the insistent demand for a procedure designed to effect a quantitative separation of phenacetin (acetphenetidine) and acetanilide in admixture. In searching the literature

[1] *Ber.*, **22**, 2990 (1899).
[2] *J. Chem. Soc.*, **89**, 59 (1906).
[3] *J. prakt. Chem.*, [2] **2**, 433 (1869).