

products. The larger and more soluble fraction was shown to be phenyl-*o*-tolyl lead dibromide by a melting point and mixed melting point. The smaller less soluble fraction was not obtained entirely pure after five recrystallizations. It melted at 144–145° and a mixed melting point with di-*o*-tolyllead dibromide indicated its identity with that substance. The di-*o*-tolyllead dibromide isolated from this reaction turned purple on exposure to light, a phenomenon not observed with the pure compound.

The author wishes to express his appreciation to Professor C. S. Marvel for his many helpful suggestions.

### Summary

1. The strong tendency of organo-lead compounds to retain at least two lead-carbon linkages has been further demonstrated by the action of nitric and hydrobromic acids on phenyltri-*o*-tolyllead.

2. A new method for the preparation of certain triaryl lead halides has been described.

3. A new volumetric method for the determination of lead in aryl lead compounds has been developed.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

## THE REACTIONS OF SOME CARBONYL COMPOUNDS WITH PHENYLHYDRAZINE

BY L. CHAS. RAIFORD AND WILBUR T. DADDOW

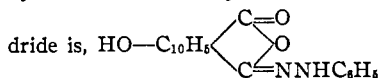
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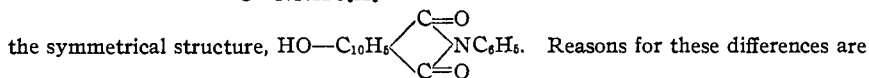
The interaction of phenylhydrazine with a carbonyl group joined directly to carbon and hydrogen (aldehydic) or to carbon and carbon (ketonic) is well known; but instances of this reaction are rare when the radical is situated between other elements. It is true that hydrazones corresponding to the last-named group of carbonyl compounds are known, but they are usually prepared by some method other than the direct<sup>1</sup> one indicated above.

The carbonyl radical in formanilide is bound directly to hydrogen and to nitrogen. A compound said to represent the hydrazone theoretically derivable from formanilide was prepared by Zwingenberger and Walther<sup>2</sup>

<sup>1</sup> The structure assigned by Anselm and Zuckmayer [*Ber.*, 32, 3294 (1899)] to the hydrazone obtained by direct action of phenylhydrazine on hydroxynaphthalic anhydride is,



In the same paper the anilide is represented by



the symmetrical structure, Reasons for these differences are not given, which raises a question regarding the first structure.

<sup>2</sup> Zwingenberger and Walther, *J. prakt. Chem.*, [2] 57, 223 (1898).

by heating methenyldiphenylamidine with an excess of phenylhydrazine. They recorded a melting point of 90–91°. Worrall<sup>3</sup> heated equimolecular proportions of phenylhydrazine and thiodiacetoacetylanilide and obtained a product melting at 126–127°. He recorded it as the hydrazone of form-anilide. In the present work in an attempt to use the direct method, formylphenylhydrazine, m. p. 143–144°,<sup>4</sup> was obtained by heating a mixture of form-anilide, phenylhydrazine and acetic acid.<sup>5</sup> The same product was obtained when form-anilide was substituted by 4-bromo-, 2-, 3-, and 4-nitroform-anilides, and by *o*- and *p*-formotoluidides, which indicates that the reaction is probably general. In each case the corresponding aniline was recovered.

A compound in which the carbonyl radical is joined directly to two nitrogen atoms is diphenylurea. Its behavior toward phenylhydrazine was next studied. When an alcoholic solution of equimolecular proportions of these compounds was heated for two days in an open vessel no new product could be detected. Repetition of the experiment in the presence of acetic acid failed to cause any change. After the mixture had been heated for thirty days, only starting material could be isolated. To test the possibility of reaction under different conditions, a mixture of diphenylurea with 1.2 molecular proportions of phenylhydrazine was heated in a sealed tube at 80–90° for seventy days. This gave 1,4-diphenylsemicarbazide; m. p. 176°. The use of an alcoholic solution of the reactants in another experiment gave almost the theoretical yield of the same product. It was identified by a mixed melting point determination with the semicarbazide prepared by the interaction of phenylhydrazine and phenyl isocyanate.<sup>6</sup>

It is known that certain sulfur compounds are more reactive than their oxygen analogs. Thus, Tiemann<sup>7</sup> found that coumarin, which contains a carbonyl radical, does not react with phenylhydrazine, while thiocoumarin does so to give the corresponding hydrazone. In the present study an attempt was made to prepare a phenylhydrazone from diphenylthiourea by refluxing an alcoholic solution of the latter with phenylhydrazine. The crystalline solid that separated on cooling melted at 178°. Aniline was isolated from the filtrate and identified by conversion into acetanilide. The other product was found by mixed melting point determination and other properties to be identical with 1,4-diphenylthiosemicarbazide,<sup>8</sup> m. p.

<sup>3</sup> Worrall, *THIS JOURNAL*, 42, 1058 (1920).

<sup>4</sup> Just [*Ber.*, 19, 1201 (1886)] reported 145° for a product obtained by heating formamide and phenylhydrazine.

<sup>5</sup> Not obtained in the absence of the acid.

<sup>6</sup> Kuhn [*Ber.*, 17, 2884 (1884)] reported 170° as the melting point.

<sup>7</sup> Tiemann, *ibid.*, 19, 1666 (1886); Meyer and Jacobson, "Lehrbuch der organischen Chemie," Veit, Leipzig, 1902, Bd. II, Th. I, p. 676.

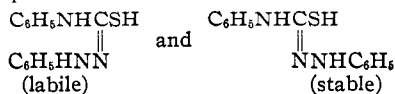
<sup>8</sup> This compound was first isolated by Fischer [*Ann.*, 190, 122 (1878)], who obtained it by mixing equimolecular proportions of phenyl mustard oil and phenylhydrazine in

178–179°, prepared by the action of phenylhydrazine on phenyl mustard oil. It was further identified by conversion into a mercury salt,<sup>9</sup> which was readily decomposed by hydrogen sulfide. Apparently this action of phenylhydrazine on thioureas is general, as indicated in Table I.

When a solution of phenylhydrazine and a thiourea is heated in the presence of a desulfurizing agent such as lead oxide, a guanidine derivative is formed. L. Marckwald<sup>10</sup> boiled an alcoholic solution of equimolecular proportions of thiocarbanilide and phenylhydrazine with an excess of lead oxide until desulfurization was complete. The product melted at 138–139°, and was assigned the structure required by the hydrazone of diphenylurea,  $(C_6H_5NH)_2C=NNHC_6H_5$  (I). The same structure was assigned by Wessel<sup>11</sup> to a product that melted at 204°, which he obtained by heating at 120° an equimolecular mixture of carbodiphenylimide and phenylhydrazine, and which he named phenylhydrazone carbodiphenylamine or hydrazone base. W. Marckwald and Wolff<sup>12</sup> also used this structure for a product that melted at 160°, and which was obtained by boiling an alcoholic solution of either of the stereoisomeric diphenylthiosemicarbazides mentioned above with aniline and lead oxide until desulfurization was complete. Their product could also be represented by formula (II),

$$\begin{array}{c} C_6H_5N \\ \diagdown \\ C \\ \diagup \\ C_6H_5NH \end{array} - NHC_6H_5$$
, which indicates a hydrazine rather than a hydrazone. The choice between these formulas involves both the method of preparation and the properties of the compounds.

Though these guanidine derivatives can be prepared from the thioureas in one operation, as indicated above, it was found in the present work that Busch's<sup>13</sup> method, which involves the preparation of the carbodiphenylimide in the pure form and subsequent treatment of this with phenylhydrazine, gives the highest yield. Incidentally, this proves that the imide is the intermediate product in Marckwald's method. The behavior "not too dilute" alcoholic solution. He reported a melting point of 177°. W. Marckwald [*Ber.*, 25, 3106 (1892)] found that at a lower temperature the reaction gave a labile form, m. p. 139°, which may be isomerized by heat or treatment with acid into a stable form, m. p. 176°. He represented the two forms as stereoisomers



<sup>9</sup> Though the product here in question was obtained in but one form, the fact that it gave a mercury salt may possibly be regarded as support for Marckwald's hydrosulfide structure. *Anal. Subs.*, 0.1471: HgS, 0.0487. Calcd. for  $(C_{13}H_{13}N_3S)_2Hg$ : Hg, 29.15. Found: Hg, 28.50.

<sup>10</sup> L. Marckwald, "Das Phenylhydrazin and seine Derivate," Thesis, Berlin, 1888, p. 39.

<sup>11</sup> Wessel, *Ber.*, 21, 2272 (1888).

<sup>12</sup> W. Marckwald and Wolff, *ibid.*, 25, 3116 (1892).

<sup>13</sup> Busch, *ibid.*, 38, 858 (1905).

of the imide toward other reagents shows that the normal reaction involves addition at one double bond, and tends to support Formula II for the product obtained when it adds phenylhydrazine. Thus, Weith<sup>14</sup> found that carbodiphenylimide may add one molecular proportion of hydrogen chloride. Lengfeld and Stieglitz<sup>15</sup> showed that this product reacts with sodium ethylate to give the ethyl ether of isodiphenylurea, which they obtained, also, by direct addition of alcohol to the diimide at an elevated temperature under pressure. Formula I would require addition at both double bonds.

If the guanidine derivatives under consideration are represented by Formula I they would be hydrazones and should not reduce Fehling's solution.<sup>16</sup> They do reduce it slightly at the boiling point. Again, if these products are hydrazones, oxidizing agents should convert them into tetrazones, as observed by Pechmann and Runge<sup>17</sup> and the molecular weights of the products should be practically double those of the starting materials. The compounds here under consideration were oxidized by mercuric oxide to new substances, but molecular weight determinations showed no difference between starting material and product, which is in accordance with the behavior expected if the starting material is represented by Formula II. Here the loss of hydrogen should occur from adjacent hydrogen atoms in the same molecule to give an azo compound. Azo compounds were obtained.

### Experimental Part

*Sym.*-di-(2,5-dibromophenyl)-thiourea.—Dyson, George and Hunter<sup>18</sup> recorded 154° as the melting point of the thiourea obtained by the action of thiocarbonyl chloride on the required dibromoaniline. In the present work the urea was first prepared by boiling an alcoholic solution of the aniline, carbon disulfide and sodium hydroxide for fourteen hours. Crystallization from benzene gave colorless needles; m. p. 191°. A second portion prepared according to Fry's<sup>19</sup> directions melted at 191°, as did a third sample obtained by the action of thiocarbonyl chloride, mentioned above.

*Anal.* Subs., 0.1718: 6.30 cc. of 0.1 N HCl. Subs., 0.2054: AgBr, 0.2828. Calcd. for C<sub>13</sub>H<sub>8</sub>N<sub>2</sub>Br<sub>4</sub>S: N, 5.14; Br, 58.82. Found: N, 5.14; Br, 58.60.

*Sym.*-di-(2,4-dibromophenyl)-thiourea.—To a solution of 8 g. of pyridine and 9.3 g. of 2,4-dibromoaniline, prepared as directed by Chattaway and Clemo,<sup>20</sup> in 100 cc. of carbon disulfide, there was added a solution of 6.4 g. of iodine in 50 cc. of carbon disulfide. After two hours, when the color of iodine had disappeared, the mixture was dis-

<sup>14</sup> Weith, *Ber.*, 7, 11 (1874).

<sup>15</sup> Lengfeld and Stieglitz, *ibid.*, 27, 926 (1894).

<sup>16</sup> Strache's [*Monatsh.*, 12, 528 (1891)] quantitative method for the determination of the carbonyl radical depends on the non-activity of phenylhydrazone toward Fehling's solution.

<sup>17</sup> Pechmann and Runge, *Ber.*, 27, 2920 (1894).

<sup>18</sup> Dyson, George and Hunter, *J. Chem. Soc.*, 443 (1927).

<sup>19</sup> Fry, *THIS JOURNAL*, 35, 1543 (1913).

<sup>20</sup> Chattaway and Clemo, *J. Chem. Soc.*, 109, 90 (1916).

tiled with steam, the non-volatile residue collected, washed with alcohol and with water. Two crystallizations from benzene gave fine needles; m. p. 203°.

*Anal.* Subs., 0.3489: AgBr, 0.4814. Calcd. for  $C_{13}H_8N_2Br_4S$ : Br, 58.82. Found: Br, 58.72.

**Preparation of Thiosemicarbazides.**—With the exceptions noted below, the general method here used was as follows: 10 g. of the required urea was suspended in alcohol, a slight excess of phenylhydrazine was added, the mixture was boiled under a reflux condenser for about six hours, and then poured into water. The method was first tested by the preparation of derivatives from phenyl-, *m*- and *p*-tolyl, and  $\beta$ -naphthylureas, which had previously been obtained by the interaction of the required amine and mustard oil, after which a number of new ones were studied. In most instances the products were readily purified by crystallization from alcohol, from which they separated as colorless needles. Physical constants and analytical data are given in Table I.

TABLE I  
THIOSEMICARBAZIDES

Name	Formula	M. p., °C.	Analyses			
			Nitrogen, %		Sulfur, %	
			Calcd.	Found	Calcd.	Found
1-Phenyl-4-(4-bromophenyl)	$C_{13}H_{12}N_2BrS$	179-180	13.05	13.08 <sup>f</sup>	9.93	9.70
1-Phenyl-4-(2,5-dibromophenyl) <sup>a</sup>	$C_{13}H_{11}N_2Br_2S$	188	10.47	10.54	...	...
1-Phenyl-4-(2,4-dibromophenyl) <sup>b</sup>	$C_{13}H_{11}N_2Br_2S$	177-178	...	...	...	...
1-Phenyl-4-( <i>o</i> -tolyl) <sup>c</sup>	$C_{14}H_{16}N_2S$	170-171	16.34	16.32	...	...
1-Phenyl-4-( <i>m</i> -tolyl) <sup>d</sup>	$C_{14}H_{16}N_2S$	173-174	16.34	16.28	...	...
1-Phenyl-4-( $\alpha$ -naphthyl) <sup>e</sup>	$C_{17}H_{16}N_2S$	192-193	14.33	14.07	10.92	10.90
1-Phenyl-4-(3-nitrophenyl)	$C_{13}H_{12}O_2N_2S$	172	...	...	11.11	11.16

<sup>a</sup> The composition was also checked by analysis for bromine. *Anal.* Subs., 0.1534: AgBr, 0.1429. Calcd. for  $C_{13}H_{11}N_2Br_2S$ : Br, 39.90. Found: Br, 39.65.

<sup>b</sup> Composition checked for halogen content. *Anal.* Subs., 0.1559: AgBr, 0.1454. Calcd. for  $C_{13}H_{11}N_2Br_2S$ : Br, 39.90. Found: Br, 39.69.

<sup>c</sup> Obtained previously by interaction of phenylhydrazine and *o*-tolyl mustard oil by Dixon [*J. Chem. Soc.*, 57, 258 (1890)], who reported a melting point of 162-163°. In the present work a solution of 10 g. of the required thiourea and 5 g. of phenylhydrazine in 250 cc. of benzene was evaporated at its boiling point to a volume of about 25 cc. and allowed to cool.

<sup>d</sup> Reported by Bose and Ray-Chaudhury [*J. Ind. Chem. Soc.*, 4, 261 (1927)], who prepared it by the action of *m*-tolyl mustard oil on phenylhydrazine. Here prepared by the method given above for the ortho isomeride.

<sup>e</sup> Checked by analysis because the product obtained by Dixon [*J. Chem. Soc.*, 61, 1019 (1892)] through the action of phenylhydrazine on  $\alpha$ -naphthyl mustard oil and supposed to be identical with this one, was recorded as melting at 183°.

<sup>f</sup> Kjeldahl method was modified as directed by Milbauer [*Z. anal. Chem.*, 42, 728 (1903)] in order to avoid loss of nitrogen.

**Preparation of Carbodiphenylimides.**—A mixture of 20 g. of the thiourea, 30 g. of lead oxide and 500 cc. of benzene was refluxed until a filtered portion no longer darkened a fresh portion of oxide, the whole filtered, the solvent distilled off until about 40-50 cc. remained, and the residue allowed to stand. The product was then purified in a suitable way. Data for the new ones thus obtained are given in Table II.

**Preparation of Diphenylanilguanidines.**—Ten grams of the required carbodiphenylimide was dissolved in about 250 cc. of benzene, the necessary amount of phenylhydrazine added, the liquid evaporated to about 25 cc. and allowed to stand. The resulting

TABLE II  
 CARBODIIMIDES

Name	Formula	M. p., °C.	Nitrogen, %	
			Calcd.	Found
Carbodi-( <i>m</i> -tolyl)	C <sub>15</sub> H <sub>14</sub> N <sub>2</sub>	118–119 <sup>a</sup>	12.61	12.72
Carbodi-(2-bromophenyl)	C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> Br <sub>2</sub>	98–100	7.95	7.83
Carbodi-(4-bromophenyl)	C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> Br <sub>2</sub>	144 <sup>b</sup>	7.95	7.91
Carbodi-(2,4-dibromophenyl)	C <sub>13</sub> H <sub>6</sub> N <sub>2</sub> Br <sub>4</sub>	156–157 <sup>c</sup>	5.49	5.48
Carbodi-(2,5-dibromophenyl)	C <sub>13</sub> H <sub>6</sub> N <sub>2</sub> Br <sub>4</sub>	172–173 <sup>d</sup>	..	..

<sup>a</sup> The residue left after evaporation of the solvent used in the method of preparation described above did not solidify on standing. Most of it boiled at 218° under 24 mm., and this distillate solidified within twenty-four hours.

<sup>b</sup> Ingold [*J. Chem. Soc.*, 125, 101 (1924)] obtained by a different method a product having the composition of this one and recorded it as a yellow viscous liquid boiling at 202° and 10 mm. The product here in question has not been reported, and is probably a polymer of Ingold's compound. Unsubstituted carbodiphenylimide was obtained by Weith [*Ber.*, 7, 10 (1874)] in both the oily and the solid forms, and Miller and Plöchl [*Ber.*, 28, 1007 (1895)] argue that the latter is a polymer of the former.

<sup>c</sup> Obtained as colorless needles from alcohol.

<sup>d</sup> Attempts to crystallize from benzene gave small compact globules that were crystalline in structure. Bromine content agrees with the formula given. *Anal.* Subs., 0.1985: AgBr, 0.2913. Calcd. for C<sub>13</sub>H<sub>6</sub>N<sub>2</sub>Br<sub>4</sub>: Br, 62.74. Found: Br, 62.46.

solid was purified in a suitable way.<sup>21</sup> Data for these derivatives are given in Table III.<sup>22</sup>

 TABLE III  
 ANILGUANIDINES<sup>o</sup>

Name	Formula	M. p., °C.	Nitrogen, %	
			Calcd.	Found
Di-( <i>o</i> -tolyl)	C <sub>21</sub> H <sub>22</sub> N <sub>4</sub>	137 <sup>a</sup>	16.96	16.93
Di-( <i>m</i> -tolyl)	C <sub>21</sub> H <sub>22</sub> N <sub>4</sub>	158–159 <sup>b</sup>	16.96	16.92
Di-(2-bromophenyl)	C <sub>19</sub> H <sub>16</sub> N <sub>4</sub> Br <sub>2</sub>	147–148 <sup>a</sup>	12.17	12.08
Di-(3-bromophenyl)	C <sub>19</sub> H <sub>16</sub> N <sub>4</sub> Br <sub>2</sub>	162–163 <sup>c</sup>	12.17	12.05
Di-(4-bromophenyl)	C <sub>19</sub> H <sub>16</sub> N <sub>4</sub> Br <sub>2</sub>	202–203 <sup>a</sup>	12.17	12.29
Di-( $\alpha$ -naphthyl)	C <sub>27</sub> H <sub>22</sub> N <sub>4</sub>	157–159 <sup>d</sup>	13.93	13.96
Di-( $\beta$ -naphthyl)	C <sub>27</sub> H <sub>22</sub> N <sub>4</sub>	181–182 <sup>e</sup>	13.93	13.90

<sup>a</sup> Colorless prisms from benzene. <sup>b</sup> Faintly colored prisms from benzene. <sup>c</sup> Colorless, fine needles from benzene. <sup>d</sup> Four recrystallizations from benzene failed to give a product with constant melting point. <sup>e</sup> All these products become colored more or less rapidly when exposed to air.

**Preparation of the Azo Compounds.**—The method was tested by starting with the unsubstituted diphenylanilguanidine isolated by Marckwald and Wolff. Five grams of the compound was dissolved in about 10 cc. of hot alcohol, an excess of mercuric oxide

<sup>21</sup> During crystallization these products often become colored, due probably to oxidation. To prevent this change Marckwald and Wolff<sup>12</sup> passed hydrogen sulfide into the crystallizing mixture. In the present work such treatment was avoided, because tests showed that when it was used the final product was contaminated with sulfur.

<sup>22</sup> It is of interest to note that no guanidine derivative was obtained from a diphenylimide which contained two bromine atoms in a single phenyl nucleus. This failure does not seem to be explainable in terms of steric hindrance. It will be studied further.

added, the mixture boiled for five to ten minutes, filtered and the azo compound isolated from the filtrate in a suitable way. The product showed the properties recorded in the literature. To show that it was not a tetrazone the molecular weight was determined.<sup>23</sup>

(a) 0.0297 g. of substance dissolved in 0.6172 g. camphor,  $\Delta = 6.7^\circ$

$$\text{Molecular weight} = \frac{(40,000)(0.0297)}{(0.6172)(6.7)} = 287$$

(b) 0.0281 g. of substance dissolved in 0.6878 g. camphor,  $\Delta = 5.5^\circ$

$$\text{Molecular weight} = \frac{(40,000)(0.0281)}{(0.6878)(5.5)} = 297$$

Calcd. for  $C_{19}H_{16}N_4$ : mol. wt., 300. Found: 287, 297.

Other compounds indicated in Table IV were obtained in the same way.

TABLE IV  
AZO COMPOUNDS FROM ANILGUANIDINES

Name	Formula	M. p., $^\circ\text{C}$ .	Nitrogen, %	
			Calcd.	Found
Di-( <i>o</i> -tolyl)	$C_{21}H_{20}N_4$	113-114 <sup>a</sup>	17.07	17.03
Di-( <i>m</i> -tolyl)	$C_{21}H_{20}N_4$	107-108 <sup>b</sup>	17.07	17.10
Di-(2-bromophenyl)	$C_{19}H_{14}N_4Br_2$	132-133 <sup>c</sup>	12.22	12.11
Di-(3-bromophenyl)	$C_{19}H_{14}N_4Br_2$	131-132 <sup>d</sup>	12.22	12.17
Di-(4-bromophenyl)	$C_{19}H_{14}N_4Br_2$	163-164 <sup>e</sup>	12.22	12.22

<sup>a</sup> Pale red needles from alcohol. <sup>b</sup> Brilliant red needles from alcohol. <sup>c</sup> Crystallization from alcohol gave brilliant red needles that soften at about  $129^\circ$  if heated slowly. <sup>d</sup> Obtained as dull red needles when the hot saturated alcoholic solution was diluted with hot water until precipitation began, and then allowed to cool. <sup>e</sup> Red crystalline material from the alcoholic filtrate of the reaction mixture.

### Summary and Conclusions

1. The carbonyl radical in formanilide does not condense with phenylhydrazine to give a hydrazone under the conditions studied. The products are aniline and formylphenylhydrazine. Substitution products of formanilide react similarly.

2. Diphenylurea reacts with phenylhydrazine to give a semicarbazide and eliminates aniline. The corresponding thiourea behaves in the same way.

3. Several new carbodiphenylimides have been prepared and studied. With the exception of the 2,4- and 2,5-dibromo compounds, the imides added phenylhydrazine to give the corresponding anilguanidines. These failures are not explainable on the theory of steric hindrance.

4. The evidence indicates that these guanidine derivatives are not hydrazones.

5. Further work is in progress.

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<sup>23</sup> Rast, *Ber.*, **55**, 3727 (1922).