

### Summary

The following new compounds have been prepared; 4-methoxyanthrone-9, 2-, 3- and 4-methoxy-9-phenylanthracene, 2-, 3- and 4-methoxy-9-hydroxy-9-phenylanthrone-10 and 2-, 3-

and 4-methoxy-9-methoxy-9-phenylanthrone-10.

The interaction of 4'-methoxy- and 4',4'-dimethoxydiphenylphthalin with thionyl chloride and the action of sulfuric acid on 4'-methoxydiphenylphthalin has been investigated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

## The Preparation and Hydrolysis of Mono- and Disubstituted Benzoylthioureas<sup>1</sup>

BY IRWIN B. DOUGLASS AND F. B. DAINS

Benzoyl isothiocyanate unites readily with most<sup>2</sup> primary and secondary amines to form substituted benzoylthioureas. From these compounds the benzoyl group can be removed by hydrolysis leaving the corresponding mono- or  $\alpha,\alpha$ -disubstituted thiourea. This hydrolysis is readily accomplished in the case of those thioureas derived from primary amines, but less readily with those from secondary.

for the rapid preparation of monosubstituted thioureas.

### Experimental

Benzoyl isothiocyanate and thioureas were prepared by a method already described.<sup>3</sup>

Hydrolysis of the monosubstituted benzoylthioureas was accomplished by boiling for five minutes with 10% sodium hydroxide. After neutralizing and making the cooled solutions faintly basic with ammonia the monosub-

#### MONOSUBSTITUTED BENZOYLTHIOUREAS

No.	Compound, thiourea	Formula	M. p., °C.	N analyses, %	
				Calcd.	Found
I	$\alpha$ -Benzoyl- $\beta$ -( <i>o</i> -chlorophenyl)-	C <sub>14</sub> H <sub>11</sub> ClN <sub>2</sub> OS	145-146	9.64	9.65
II	$\alpha$ -Benzoyl- $\beta$ -( <i>p</i> -chlorophenyl)-	C <sub>14</sub> H <sub>11</sub> ClN <sub>2</sub> OS	140	9.64	9.74
III	$\alpha$ -Benzoyl- $\beta$ -(2,4-dichlorophenyl)-	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> OS	152-153	8.62	8.41
IV	$\alpha$ -Benzoyl- $\beta$ -(3,4-dichlorophenyl)-	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> OS	155-156	8.62	8.61
V	$\alpha$ -Benzoyl- $\beta$ -(2,5-dichlorophenyl)-	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> OS	189-190	8.62	8.75
VI	$\alpha$ -Benzoyl- $\beta$ -( <i>p</i> -bromophenyl)-	C <sub>14</sub> H <sub>11</sub> BrN <sub>2</sub> OS	149-150	8.36	8.50
VII	$\alpha$ -Benzoyl- $\beta$ -(2,4-dibromophenyl)-	C <sub>14</sub> H <sub>10</sub> Br <sub>2</sub> N <sub>2</sub> OS	160-161	6.75	6.75
VIII	$\alpha$ -Benzoyl- $\beta$ -(2,6-dibromo-4-methylphenyl)-	C <sub>16</sub> H <sub>12</sub> Br <sub>2</sub> N <sub>2</sub> OS	195-196	6.55	6.46
IX	$\alpha$ -Benzoyl- $\beta$ -(2,4,6-tribromophenyl)-	C <sub>14</sub> H <sub>9</sub> Br <sub>3</sub> N <sub>2</sub> OS	206-208	5.68	5.76
X	$\alpha$ -Benzoyl- $\beta$ -( <i>p</i> -iodophenyl)-	C <sub>14</sub> H <sub>11</sub> IN <sub>2</sub> OS	154	7.33	7.35
XI	$\alpha$ -Benzoyl- $\beta$ -( <i>p</i> -fluorophenyl)-	C <sub>14</sub> H <sub>11</sub> FN <sub>2</sub> OS	126-127	10.22	10.14
XII	$\alpha$ -Benzoyl- $\beta$ -( <i>o</i> -nitrophenyl)- <sup>a</sup>	C <sub>14</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> S	138-139 S	10.64	10.91
XIII	$\alpha$ -Benzoyl- $\beta$ -( <i>o</i> -hydroxyphenyl)-	C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> S	216	10.30	10.17
XIV	$\alpha$ -Benzoyl- $\beta$ -( <i>p</i> -hydroxyphenyl)-	C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> S	171-172	10.30	10.28
XV	( $\beta$ -Benzoylthioureido)-benzoic acid	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> S	223 dec.	9.33	9.36

<sup>a</sup> Neither this compound nor the corresponding *m*-nitro derivative underwent satisfactory hydrolysis.

#### DISUBSTITUTED BENZOYLTHIOUREAS

No.	Compound, thiourea	Formula	M. p., °C.	N analyses, %	
				Calcd.	Found
XVI	$\beta$ -Benzoyl- $\alpha$ -methyl- $\alpha$ -phenyl-	C <sub>15</sub> H <sub>14</sub> ON <sub>2</sub> S	138-139	10.37	10.44
XVII	$\beta$ -Benzoyl- $\alpha$ -benzyl- $\alpha$ -phenyl-	C <sub>21</sub> H <sub>18</sub> N <sub>2</sub> OS	156-157	8.09	8.00
XVIII	$\beta$ -Benzoyl- $\alpha$ -methyl- $\alpha$ -( <i>p</i> -tolyl)-	C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> OS	124-125	9.86	9.93
XIX	$\beta$ -Benzoyl- $\alpha$ -methyl- $\alpha$ -( <i>m</i> -tolyl)-	C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> OS	133-134	9.86	9.82
XX	$\beta$ -Benzoyl- $\alpha$ -methyl- $\alpha$ -( <i>o</i> -tolyl)-	C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> OS	119-120	9.86	9.82
XXI	$\beta$ -Benzoyl- $\alpha$ -ethyl- $\alpha$ -( <i>p</i> -tolyl)-	C <sub>17</sub> H <sub>18</sub> N <sub>2</sub> OS	136	9.40	9.43

Since the benzoyl isothiocyanate and acyl thioureas are easily made, the procedure affords a method for the identification of amines and also

stituted thioureas separated and were removed by filtering.<sup>4</sup> The yields were 80-90%.

Disubstituted benzoylthioureas were more difficult to

(1) From part of a thesis presented by Irwin B. Douglass in partial fulfillment of the requirements for the Ph.D. degree.

(2) Benzoyl isothiocyanate could not be induced to react with 2,4-dinitroaniline, 2,4,6-trinitroaniline, or 2,6-dibromo-4-nitroaniline.

(3) Douglass and Dains, *THIS JOURNAL*, **56**, 719 (1934).

(4) This investigation was confined to thioureas derived from aryl amines. The recovery of monosubstituted alkylthioureas is less satisfactory.

hydrolyze.<sup>5</sup> When subjected to the treatment just described they were recovered practically unchanged. The following method gave the best results.

Ten grams of the thiourea, with an exactly equivalent amount of sodium hydroxide, were added to 100 cc. of alcohol and the mixture was refluxed for eight to ten hours. The alcohol was removed by steam and the oil and water remaining were allowed to stand for several days. The crystallized thiourea was filtered off and recrystallized from dilute alcohol. Acidification of the filtrate brought down unchanged starting compound and benzoic acid. The yields were less than 45%.

In the table are listed the new benzoylthioureas prepared. Unless otherwise stated the compounds were hydrolyzed and the products identified by melting points and analyses. To illustrate:  $\alpha$ -benzoyl- $\beta$ -(*o*-chlorophenyl)-thiourea, I, yielded on hydrolysis *o*-chlorophenylthiourea. A few of the monosubstituted thioureas prepared in this way were:

**2,5-Dichlorophenylthiourea**, m. p. 192–193°. <sup>6</sup> *Anal.* Calcd. for  $C_7H_6Cl_2N_2S$ : N, 12.68. Found: N, 12.53.

(5) Dixon, *J. Chem. Soc.*, **67**, 1044 (1895); **85**, 811 (1904).

(6) Cf. Capps and Dehn, *THIS JOURNAL*, **54**, 4304 (1932).

**3,4-Dichlorophenylthiourea**, m. p. 203–204°. <sup>7</sup> *Anal.* Calcd. for  $C_7H_6Cl_2N_2S$ : N, 12.68. Found: N, 12.57.

**2,6-Dibromo-4-methylphenylthiourea**, m. p. 221–222°. *Anal.* Calcd. for  $C_8H_8Br_2N_2S$ : N, 8.65. Found: N, 8.58.

**2,4,6-Tribromophenylthiourea**, m. p. 217°. *Anal.* Calcd. for  $C_7H_5Br_3N_2S$ : N, 7.28. Found: N, 7.26.

***p*-Thioureidobenzoic acid**,<sup>8</sup> m. p. 255°. *Anal.* Calcd. for  $C_8H_8N_2O_2S$ : N, 14.29. Found: N, 14.24.

### Summary

A method of preparing certain mono- and  $\alpha,\alpha$ -disubstituted thioureas by the hydrolysis of the corresponding benzoyl derivatives has been described.

A number of new derivatives of benzoyl isothiocyanate are reported. Since these compounds are readily prepared from the amines they will prove useful in their identification.

(7) Cf. Dyson, George and Hunter, *J. Chem. Soc.*, **129**, 3042 (1926).

(8) Listed in the Centrallblatt Formel Register for 1927 but cf. Dyson, George and Hunter, *ibid.*, **130**, 442 (1927).

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## Tetrachlorophthalimide as a Reagent in Qualitative Organic Analysis

BY C. F. H. ALLEN AND R. V. V. NICHOLLS

Potassium tetrachlorophthalimide has been found to be a suitable reagent to use in the identification of a wide variety of halogen compounds. It is superior to the 3-nitrophthalimide<sup>1</sup> because it is less expensive, and gives higher melting derivatives. It is not limited to the identification of alkyl halides, as are the procedures that make use of the Grignard reagent.<sup>2</sup> The new reagent reacted readily with the alkyl halides, the straight-chain  $\alpha$ -halogen esters, the high-boiling chloroformates, the halohydrins, halo ketones, and halo ethers which were studied. With halogen derivatives that boil below 140° the reaction had to be carried out in a sealed tube. The reagent did not combine with  $\alpha$ -bromo derivatives of ethyl isobutyrate and isovalerate. With the low-boiling chloroformates, no reaction occurred at the boiling point and explosions resulted when sealed tubes were used. Ethyl  $\beta$ -chloropropionate gave no derivative.

Anomalous results were obtained with three halogen derivatives.  $\gamma$ -Chlorobutyrophenone

gave benzoylcyclopropane, on treatment with the reagent. Ethyl bromomalonate lost one carbethoxy group and gave the same derivative that was obtained from ethyl chloroacetate. Bromotricarbomethoxymethane lost all three carbomethoxy groups, and gave the N-methylimide, m. p. 210–211°.

### Experimental

**Tetrachlorophthalimide.**—A finely ground, intimate mixture of 30 g. of tetrachlorophthalic anhydride<sup>3</sup> and 11 g. of U. S. P. ammonium carbonate in a 400-cc. Pyrex beaker, covered by a piece of cardboard or a watch glass with a hole through which passes a heavy glass stirring rod, is slowly heated with occasional stirring until the mass becomes molten. After cooling, the solid is pulverized and recrystallized from 150 cc. of nitrobenzene, washing with ether to remove the excess solvent. The imide thus prepared weighs 27 g. (91% yield) and melts at 336–337°.

*Anal.* Calcd. for  $C_8HO_2NCl_4$ : N, 4.9; Cl, 49.8. Found: N, 5.1, 5.1; Cl, 49.7.

**Potassium Derivative.**—A solution of 1.6 g. of potassium hydroxide in 20 cc. of dry methyl alcohol is added to a solution of 8 g. of the imide in 200 cc. of boiling dioxane (dried by refluxing over sodium). After cooling rapidly,

(1) Sah and Ma, *Ber.*, **65**, 1630 (1932).

(2) Marvel, Gauerke and Hill, *THIS JOURNAL*, **47**, 3009 (1925); Hill, *ibid.*, **50**, 187 (1928); Gilman and Furry, *ibid.*, **50**, 1214 (1928); Schwartz and Johnson, *ibid.*, **53**, 1063 (1931).

(3) The necessary tetrachlorophthalic anhydride was supplied by the National Aniline and Chemical Co., and is gratefully acknowledged.