

The 1,3-dimethyl-4-*t*-butylbenzene and the 1,3-dimethyl-4-*s*-butylbenzene both undergo rearrangement on treatment with aluminum chloride to give 1,3-dimethyl-5-*t*-butylbenzene. The identity of the 1,3,5-hydrocarbon formed by these rearrangements was established by means of melting points of mixtures of the trinitro derivatives and by freezing points of mixtures of rearrangement product with an authentic sample of the

1,3,5-hydrocarbon synthesized by the Friedel-Crafts reaction.

The 1,3-dimethyl-4-isobutylbenzene on treatment with aluminum chloride yields a mixture of hydrocarbons.

The 1,3-dimethyl-4-*n*-butylbenzene and aluminum chloride yields 1,3-dimethyl-5-*s*-butylbenzene.

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## Phenylpropiol-4-chlorothioanilide

BY DAVID E. WORRALL AND EDWARD LAVIN

The thioamide obtained by the condensation of sodium phenylacetylene with phenyl isothiocyanate has been shown to react characteristically<sup>1</sup> with hydroxylamine and hydrazine. Since the resulting isoxazole or pyrazole, as the case may be, contains replaceable hydrogen both in the heterocyclic ring (position 4) and in the aniline ring, the reaction has been found useful for the synthesis of certain derivatives.<sup>2</sup> The present investigation is concerned with the reactions of chlorinated thioanilides of this series.

### Experimental

**Phenylpropiol-4-chlorothioanilide (I).**—To 0.25 gram mole of sodium phenylacetylene suspended in ether was added an equivalent amount of *p*-chlorophenyl isothiocyanate. The mixture, after standing overnight, was worked up in the customary manner, yielding after thorough washing with cold alcohol approximately 50 g. of material. A small portion was recrystallized from alcohol, separating as yellow plates, m. p. 138–139° with decomp.

*Anal.* Calcd. for C<sub>15</sub>H<sub>10</sub>ClNS: C, 66.3; H, 3.7. Found: C, 66.4; H, 3.5.

**bis-Phenylpropiol-4-chloroanilide.**—Heat alone even at 100° changed I into a black tar that on cooling hardened into a glossy black resin. The dimer obtained by heating an ether solution of I in the presence of alkali, separated after several hours as a dark green crystalline mass. It was thoroughly washed with hot alcohol; m. p. 245–246°, dec.

*Anal.* Calcd. for (C<sub>15</sub>H<sub>10</sub>ClNS)<sub>2</sub>: C, 66.3; H, 3.7. Found: C, 66.3; H, 3.9.

A poor yield of the dibromide of I was obtained from the polymer suspended in chloroform. Yellow crystals melting with decomposition at 229–230° separated.

*Anal.* Calcd. for C<sub>15</sub>H<sub>10</sub>Br<sub>2</sub>ClNS: C, 41.6; H, 2.5. Found: C, 41.3; H, 2.6.

**3-(4-Chloroanilino)-5-phenylisoxazole (II).**—Using an excess of hydroxylamine with 10 g. of I, a product was obtained that eventually, after repeated crystallizations from alcohol, formed nearly colorless plates, m. p. 166–167°; yield 1.5–2 g.

*Anal.* Calcd. for C<sub>15</sub>H<sub>11</sub>ClN<sub>2</sub>O: C, 66.5; H, 4.1. Found: C, 66.8; H, 4.6.

**1-Phenacyl-5-chlorobenzothiazole.**—A small amount of insoluble material separated from the isoxazole preparation. It crystallized from glacial acetic acid as scarlet needles, melting with decomposition at 192–193°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>10</sub>ClNOS: C, 63.1; H, 3.5. Found: C, 62.6; H, 3.5.

**3-(2-Bromo-4-chloroanilino)-4-bromo-5-phenylisoxazole.**—To 0.5 g. of II dissolved in warm chloroform was added a slight excess of bromine. Tufts of white needles separated on cooling, m. p. 133–134°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>9</sub>Br<sub>2</sub>ClN<sub>2</sub>O: Br, 37.3. Found: Br, 37.5.

**3-(2,4-Dichloroanilino)-4-chloro-5-phenylisoxazole.**—Dry air was blown through a chloroform solution of II which previously had been saturated with chlorine. The residue separated from ligroin in the form of needles slightly discolored; m. p. 95–96°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>9</sub>Cl<sub>3</sub>N<sub>2</sub>O: Cl, 31.4. Found: Cl, 31.2.

**3-(2-Nitro-4-chloro)-4-nitro-5-phenylisoxazole.**—A small portion of II dissolved in nitric acid and precipitated by water crystallized from glacial acetic acid as pale yellow plates, m. p. 165–166°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>9</sub>ClN<sub>4</sub>O<sub>2</sub>: C, 50.0; H, 2.5. Found: C, 49.9; H, 2.5.

**3-(4-Chloroanilino)-5-phenylpyrazole (III)** was prepared from 10 g. of I using two equivalents of hydrazine. The crude product was heated with ligroin, thus removing much of the color, after which it was crystallized several times from alcohol as cream-colored needles, m. p. 174–175°; final yield, 2.4 g.

*Anal.* Calcd. for C<sub>15</sub>H<sub>12</sub>ClN<sub>2</sub>: C, 66.8; H, 4.5. Found: C, 66.9; H, 4.4.

(1) Worrall, *THIS JOURNAL*, **59**, 933 (1937).

(2) Worrall, *ibid.*, **60**, 1198 (1938).

**3-(2-Bromo-4-chloroanilino)-4-bromo-5-phenylpyrazole.**—An insoluble salt separated from a chloroform solution of III on the addition of an excess of bromine dissolved in chloroform. It was decomposed by hot alcohol, from which the new substance separated as needles, m. p. 198–199°.

*Anal.* Calcd. for  $C_{15}H_{10}Br_2ClN_2$ : Br, 37.4. Found: Br, 37.1.

**Phenylpropiol-3-chlorothioanilide.**—Prepared from *m*-chlorophenyl isothiocyanate, it was purified in small lots by crystallization from chloroform–petroleum ether mixtures. Tiny yellow needles were obtained which melted with decomposition at 115–116°.

*Anal.* Calcd. for  $C_{15}H_{10}ClNS$ : C, 66.3; H, 3.7. Found: C, 66.8; H, 3.7.

It was readily polymerized by heating an ether solution

with a few drops of sodium hydroxide solution. The new substance separated in the form of brown crystals, melting with decomposition at 227–228°.

*Anal.* Calcd. for  $(C_{15}H_{10}ClNS)_x$ : C, 66.3; H, 3.7. Found: C, 66.3; H, 3.7.

### Summary

Phenyl propiol-chlorothioanilide, prepared by the interaction of sodium phenylacetylene and *p*-chlorophenyl isothiocyanate, reacts with hydroxylamine and hydrazine. The resulting isoxazole and pyrazole form substitution products with bromine, chlorine and nitric acid.

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## Reactions of Phenylpropiol-4-iodoanilide and Similar Thioamides

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In a previous investigation<sup>1</sup> it was shown that the isoxazole and pyrazole obtained from the condensation of phenylacetylene with phenyl isothiocyanate form substitution products with chlorine, bromine and nitric acid. The reaction has been investigated further in order to find the scope, for it not only offers a new approach to the isoxazole or pyrazole series but also furnishes a new series of derivatives.

Theoretically, substitution in these compounds may occur in the phenyl, anilino and pyrazole or isoxazole rings. Actually, as the presence of benzoic acid<sup>1</sup> among the oxidation products of a halogenated isoxazole indicated, reactivity is confined to the anilino or heterocyclic ring or both. That the latter group is involved follows from the fact that the thioamide obtained from *p*-bromoisothiocyanate formed an isoxazole isomeric with that resulting from the bromination of anilinophenylisoxazole.<sup>1</sup> It also follows that substitution starts with the isoxazole ring and at position 4. The oxidation of the tribromo derivative of the corresponding pyrazole<sup>1</sup> produced 2,4-dibromoaniline which fits in with this picture and which also indicates that the anilino group reacts in the orthodox manner with bromine. It has been assumed that similar relations exist with the substances investigated in the present communication.

(1) *THIS JOURNAL*, 60, 1198 (1938).

### Experimental

The thioamides were prepared through the interaction of sodium phenylacetylene suspended in ether with the appropriate isothiocyanate. The product after standing for several hours was filtered and cautiously decomposed with ice water and dilute acid. Since these amides are easily destroyed even by moderate heating, the crude product after thorough washing with cold alcohol was used for the experimental work. Small portions were purified for analysis by the use of chloroform–petroleum ether mixtures. Save for the 4-phenyl derivative which formed bright yellow plates, pale yellow needles were obtained. All melted with decomposition. Yields (60–80%) were satisfactory except for the phenethyl derivative. The substances were polymerized by heating ether solutions in the presence of a few drops of concd. sodium hydroxide solution. Brown or greenish-brown irregular platelets formed which melted with decomposition.

TABLE I  
ANILINE SUBSTITUTED PHENYLPROPIOL THIOANILIDES

Subs.	M. p., °C.	Formula	Analyses, %	
			Calcd.	Found
4-Iodo Dimer	140–141 Indefinitely above 173	$C_{15}H_{10}INS$	8.8	8.8
4-Ethoxy Dimer	111–112 199–200	$(C_{14}H_{10}INS)_x$ $(C_{17}H_{15}NOS)_x$	11.4	11.4
3-Bromo Dimer	120–121 Indefinite	$C_{15}H_{10}BrNS$ $(C_{15}H_{10}BrNS)_x$	10.1	10.4
4-Phenyl Dimer	128–129 230–232	$C_{21}H_{15}NS$ $(C_{21}H_{15}NS)_x$	10.2	10.4
$\alpha$ -Naphthylamide	184–185	$C_{19}H_{13}NS$	11.2	10.9

The isoxazoles were obtained by gradually adding the thioamide to an excess of hydroxylamine in hot alcohol until evolution of hydrogen sulfide stopped. The dark colored solution was then concentrated to a small volume.