

160° under 2 mm. pressure against a tube cooled with acetone and dry ice. Clear, feathery needles were obtained which melted at 187.5–188.5° (corr.). The poorest yield of sublimed iretol was 40%, and the best was 75% of the theoretical amount.

Anal. Calcd. for $C_7H_8O_4$: C, 53.83; H, 5.17; methoxyl, 19.87. Found: C, 54.10; H, 5.38; methoxyl (Zeisel), 19.60.

Iretol is stable when pure and dry, but readily turns dark if exposed to moisture and oxygen.

Summary

2,4,6-Trinitroanisole may be satisfactorily reduced catalytically to give 68 to 81% yields of 2,4,6-triaminoanisole, provided the reduction is carried out rapidly. The triamine may be hydrolyzed to 2,4,6-trihydroxyanisole (iretol) in 40 to 75% yields by means of hydrochloric acid.

URBANA, ILL.

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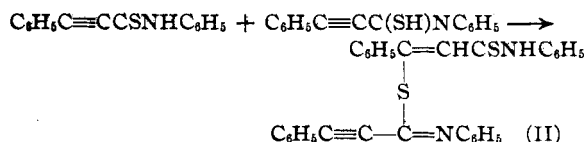
[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY, TUFTS COLLEGE]

The Action of Hydroxylamine and Hydrazine on Acetylenic Thioamides

BY DAVID E. WORRALL

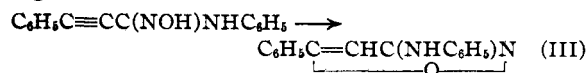
It has been shown previously that sodium phenylacetylene forms addition products with aromatic isothiocyanates.¹ Since the resulting thioamides contain an acetylenic group, they behave in a characteristic manner with certain reagents. These reactions have been investigated in the present communication.

Phenylpropiol thioanilide¹ obtained from phenyl isothiocyanate is destroyed easily by heat or acids; consequently the addition of water to the acetylenic group is yet to be observed. Like any thioamide it is soluble in aqueous alkali. On warming it polymerizes, a change that has been assumed to result from the interaction of I with its enol



The product is a highly colored dimer, still soluble in alkali, which reacts with hydroxylamine through hydrogen sulfide elimination. With bromine, part of the molecule is converted into the dibromide of I. The other portion changes into an intractable tar, precisely the effect of bromine on I, accompanied by the formation of hydrogen bromide.

I also reacts in a characteristic manner with hydroxylamine, the first formed oxime rearranging into an isoxazole.



III reacts smoothly with nitric acid and with bromine, forming products in which substitution

has taken place in the aniline group, evidenced by the production of benzoic acid on oxidation. In a similar manner hydrazine and phenylhydrazine lead to substituted pyrazoles. The pyrazole obtained from hydrazine is of such a nature that the aniline group present is capable of reacting with three equivalents of bromine or nitric acid.

A small amount of by-product is usually present in the preparation of III, the analysis of which indicates that the original substance has taken on one equivalent of oxygen. Since the aromatic thioamides are readily converted into thiazoles under mild oxidizing conditions, the substance² may be regarded as phenacyl benzothiazole, $C_6H_5COCH_2C \equiv \text{NC}_6H_5$. It results perhaps from the addition of hydroxylamine to the acetylenic group followed by oxidation and hydrolysis under the influence of the organic base.

Experimental

Phenylpropiol Thioanilide.—To 0.5 gram mole of phenylacetylene converted into the sodium derivative and suspended in dry ether was added the equivalent of phenyl isothiocyanate. The bulky product after several hours was filtered and washed with ether. The residue was decomposed immediately in small lots (unchanged sodium present) with a well-stirred mixture of ice and water. An excess of dilute acid was used to complete the reaction after which the product, following thorough washing with dilute alcohol, was suspended in chloroform. Petroleum ether in excess was then added; final yield 70 g. Because of destructive decomposition, heating must be avoided. It separated from warm chloroform-petroleum ether mixtures as tiny yellow needles, decomposing at 113–114°. *Anal.* Calcd. for $C_{15}H_{11}NS$: C, 75.9; H, 4.6; S, 13.5. Found: C, 75.5; H, 4.6; S, 13.7. It changes into a glossy black resin if heated to 100° for a few minutes. The thio-

(1) Worrall, *THIS JOURNAL*, **39**, 697 (1917).

(2) Jacobsen, *Ber.*, **21**, 2629 (1888).

anilide is soluble in aqueous alkali, precipitating out unchanged on neutralization with acid, but polymerizing on the application of heat. A similar change takes place more slowly on heating an alcoholic solution of the substance in the absence of alkali accompanied by considerable decomposition into hydrogen sulfide and an intractable black tar. Destructive decomposition occurs slowly at room temperature if an acid is added to the alcoholic solution. All attempts to obtain a ketone by hydration of the acetylenic group failed. Mercuric salts decompose the substance. Bromine reacts instantly with blackening of the solution and subsequent elimination of hydrogen bromide fumes. An odor similar to sulfur chloride was noticed in the tarry residue.

Bis-phenylpropylthioanilide was obtained by heating I with alcohol under a reflux condenser for several hours. The lustrous bronze colored plates produced were filtered while hot and thoroughly washed with warm alcohol; yield approximately 40%. *Anal.* Calcd. for $(C_{15}H_{11}NS)_2$: C, 75.9; H, 4.6. Found: C, 75.8; H, 4.6. A molecular weight determination using bromoform as a solvent indicated a dimer. It sinters at about 250°, decomposing indefinitely. Hydrogen sulfide was eliminated slowly by the action of hydroxylamine. The tarry residue on examination was found to contain sulfur, although no definite substance was isolated.

Phenylpropylthioanilide Dibromide.—An equal weight of bromine mixed with II suspended in chloroform caused crystal formation in a few minutes. On standing, copious evolution of hydrogen bromide fumes occurred, but the amount of solid material did not change noticeably. Most of the products of the reaction remained in solution and were discarded, as tars separated on evaporation. The crystalline material separated from a large volume of glacial acetic acid in small yellow plates, decomposing at 226–227°. *Anal.*³ Calcd. for $C_{15}H_{11}NSBr_2$: C, 45.3; H, 2.8; Br, 40.3. Found: C, 45.5; H, 2.7; Br, 40.2.

3-Anilino-5-phenylisoxazole.—An alcohol solution containing three equivalents of hydroxylamine was mixed with 10 g. of I and slowly heated to the boiling point. Heating was continued under a reflux condenser until no further hydrogen sulfide evolution occurred. The red solution, filtered if necessary, was poured into water. The product was crystallized repeatedly from alcohol to remove colored impurities, finally separating as sparkling plates, m. p. 142–143°; yield approx. 2 g. *Anal.* Calcd. for $C_{15}H_{12}ON_2$: C, 76.2; H, 5.1. Found: C, 76.1; H, 5.2. It is unchanged after long heating with either acid or alkali, but readily reduces permanganate solutions.

I-Phenacyl Benzothiazole.—A substance insoluble in alcohol was obtained with the isoxazole if concentrated solutions were used; yield 0.4 g. It was crystallized from glacial acetic acid in the form of deep yellow needles decomposing at 190–191°. *Anal.* Calcd. for $C_{15}H_{11}ONS$: C, 71.1; H, 4.3; S, 12.6. Found: C, 70.8; H, 4.4; S, 12.5. It is soluble in alcoholic potash, from which it is precipitated unchanged by acid or dilution with water.

(3) Low results occur in determination of bromine by the Carius method unless precautions are taken, as nitric acid promptly liberates hydrogen bromide from the substance.

Hot alcoholic potash decomposes it into a tar. A small amount of an oil soluble in acid and with a pyridine-like odor was obtained on long heating with hydrochloric acid.

3-*p*-Bromoanilino-5-phenylisoxazole.—The isoxazole was brominated in chloroform and crystallized from alcohol, separating as plates, m. p. 158°. *Anal.* Calcd. for $C_{15}H_{11}ON_2Br$: Br, 25.4. Found: Br, 25.5. On oxidation with permanganate, benzoic acid was isolated from the material insoluble in acetone.

3-[2,4-Dinitroanilino]-5-phenylisoxazole.—The isoxazole dissolved readily in concd. nitric acid. Water throws out of solution the product which separated from glacial acetic acid as glittering yellow plates, m. p. 245–246°. *Anal.* Calcd. for $C_{15}H_9O_5N_4$: C, 55.5; H, 2.8. Found: C, 55.9; H, 2.8.

3-Anilino-5-phenylpyrazole.—I (10 g.) was heated with two equivalents of hydrazine, the excess being necessary to avoid the formation of II. Nearly colorless needles, m. p. 151–152°, were obtained eventually by repeated crystallization of the crude product; yield 3–4 g. The hydrochloric acid salt, prepared by adding a few drops of concd. acid to the alcohol solution, m. p. 166–167°, was used for analysis. *Anal.* Calcd. for $C_{15}H_{13}N_3HCl$: C, 66.3; H, 5.2. Found: C, 66.5; H, 5.2. The base is sparingly soluble in hot water and unaffected by hot acid or alkali.

3-[2,4,6-Tribromoanilino]-5-phenylpyrazole.—The tribromo derivative, obtained as before, separated as a salt that hydrolyzed in the presence of alcohol or water. It was crystallized from a large volume of alcohol, forming needles decomposing at 206–207°. *Anal.* Calcd. for $C_{15}H_9N_3Br_3$: C, 38.1; H, 2.1. Found: C, 38.4; H, 2.3. On extraction with hot water of the acetone-insoluble material obtained by oxidation with permanganate, two products were found, benzoic acid and a yellow bromine-containing substance that was not examined further.

3-[2,4,6-Trinitroanilino]-5-phenylpyrazole.—Nitric acid dissolved the pyrazole, yielding a product that was crystallized from glacial acetic acid. It forms lustrous yellow needles decomposing at 266°. *Anal.* Calcd. for $C_{15}H_9N_6O_6$: C, 48.6; H, 2.7. Found: C, 48.3; H, 3.1.

1-Phenyl-3-anilino-5-phenylpyrazole.—Obtained from two equivalents of phenylhydrazine with 10 g. of I as pointed prisms, m. p. 153–154°, yield 4 g. *Anal.* Calcd. for $C_{21}H_{17}N_3$: C, 81.0; H, 5.5. Found: C, 81.4; H, 5.4. The dibromo derivative, needles, m. p. 181°, and the trinitro, tiny yellow plates, m. p. 197–198°, were prepared and analyzed.

Summary

Phenyl isothiocyanate forms an unsaturated thioanilide with phenylacetylene, a substance easily destroyed by acids, free halogens or heat. It is polymerized by alkali and reacts with hydroxylamine, hydrazine and phenylhydrazine, forming heterocyclic compounds from which bromo and nitro derivatives have been prepared.

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