This product is identical with the dimethyl ether of phenoltetrachlorophthalein obtained by Orndorff and Black[1] by a different method.

Summary.

1. A formula for phenolphthaleinoxime has been given which explains its quantitative decomposition into *p*-hydroxybenzoyl-*o*-benzoic acid and *p*-aminophenol and which is in better accord with all of the facts known in regard to the oxime than any other which has been proposed.
2. The preparation of phenolphthalein and of several mixed phthaleins from *p*-hydroxybenzoyl-*o*-benzoic acid has been accomplished.
3. Strong evidence has been obtained to show that the condensation of phenol and phthalic anhydride to give phenolphthalein takes place in two stages and that *p*-hydroxybenzoyl-*o*-benzoic acid is an intermediate product in this condensation.
4. The mixed phthaleins, like phenolphthalein itself, are purified with difficulty. It was found best to make and purify the acetates and by hydrolyzing the latter obtain the pure phthaleins.
5. The acetates of the phenolresorcinolphthaleins and of α-naphtholphenolphthalein have been obtained pure.
6. The anilide of phenolanilinephthalein is formed instead of the phthalein when *p*-hydroxybenzoyl-*o*-benzoic acid is heated with aniline.
7. The two phenolresorcinolphthaleins have been obtained pure by hydrolyzing a mixture of the pure triacetates.
8. The product of the condensation of two molecules of *p*-hydroxybenzoyl-*o*-benzoic acid with the loss of a molecule of water has been studied. This ether-like anhydride resembles the phthaleins very closely and decomposes into phenolphthalein and phthalic acid anhydride when heated.
9. *p*-Methoxybenzoyl-*o*-tetrachlorobenzoic acid, and its sodium, and its potassium salts have been prepared and studied.
10. The acetate of *p*-methoxybenzoyl-*o*-tetrachlorobenzoic acid condenses with phenols to give the monomethyl ethers of the phthaleins. It probably possesses a lactone structure.

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THE ACTION OF THE TOLYL MUSTARD OILS ON SODIUMPHENYLACETYLENE.

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It has long been known that the thioanilids react readily with hydroxylamine[2] through the elimination of hydrogen sulfide to form oximes.

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[1] *Am. Chem. J.*, 41, 374 (1909).

[2] Müller, *Ber.*, 19, 1669 (1886).

If the thioanilids or other substituted thioamids contain an acetylene group in the 2 position with regard to sulfur, the oxime formation might be expected to be followed by a rearrangement to a heterocyclic carbon-nitrogen ring. Such rearrangements have been observed by Moureau and Brachin as a result of the action of hydroxylamine[1] and the hydrazines[2] on certain ketone derivatives of phenylacetylene. Thioacetylenic compounds of this type have recently been made available[3] through the condensation of sodiumphenylacetylene and phenyl mustard oil, the product of which was found to react in the desired manner. The synthesis of these unsaturated thioamids has been continued, as the reaction with the above mentioned bases appeared to be a promising method for the preparation of substituted amino isoxazols and pyrazols.

The tolyl mustard oils were found to condense with sodiumphenylacetylene, yielding on addition of acid the thiotoluid. The transformations are expressed as follows:

$$C_6H_5C \equiv C - Na + CH_3C_6H_4NCS \longrightarrow C_6H_5C \equiv$$
$$CCS - Na.NC_6H_4CH_3 + HCl \longrightarrow C_6H_5C \equiv CCSNHC_6H_4CH_3$$

The *p* mustard oil condensed very smoothly, but the *m* and *o* compounds did not react as readily, and in the latter case no crystalline derivative was isolated. The thiotoluids reacted readily with both hydroxylamine and phenylhydrazine, hydrogen sulphide forming as soon as the bases were added. Considerable decomposition took place, however, because of side reactions and the yields were always poor. This was especially true with phenylhydrazine which reacted in such a way that a tar invariably formed.

The investigation of the action of these organic bases on thioamids will be continued. Work is under way with the thioamids of acetoacetic and acetondicarboxylic esters.

Experimental Part.

Phenylacetylene was prepared by the method of Nef.[4] Cinnamic acid was brominated and then treated successively with aqueous soda solution and alcoholic potash. The final product was fractionated in vacuum and then an ordinary pressure, yielding a colorless liquid of nearly constant boiling point. The sodium derivative was prepared by the action of phenylacetylene on granulated sodium[5] suspended in ether. The tolyl isothiocyanates were easily prepared in good yield by the condensation of the corresponding toluidine with carbon disulphide and sub-

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[1] *Bull. soc. chim.*, [3] 31, 343 (1904).

[2] *Compt. rend.*, 136, 1262 (1903).

[3] This work, which was done in the laboratory and under the direction of Prof. Michael, has not been published as yet.

[4] *Ann.*, 308, 265 (1899).

[5] Brühl, *Ber.*, 35, 3516 (1902).

sequent decomposition of the product by heating with phosphoric acid. The mixture in each case was distilled with steam and the distillate refractionated.

Phenylpropiolthio-*p*-toluid, $C_6H_5C \equiv CCSNHC_6H_4CH_3$.—Five grams of phenylacetylene were converted into the sodium derivative and suspended in ten volumes of anhydrous ether. Then 7.3 g. of *p*-tolyl mustard oil were added and the mixture allowed to stand overnight at room temperature. A bulky precipitate of microscopic needle-like crystals separated out and absorbed the ether, forming a yellowish spongy mass. More ether was added and the mixture refluxed for an hour to make sure that the reaction was completed. It was filtered with the aid of a Buchner funnel, washed several times with dry ether and finally pressed between filter paper to a hard white cake. This was broken up and added a little at a time, with stirring, to a large volume of ice water. A voluminous yellow crystalline precipitate immediately separated out. A slight excess of cold dilute hydrochloric acid was added and the substance filtered. It was washed several times with water and dried in a vacuum desiccator. Yield, 9 g.

0.2 g. subst. gave 9.4 cc. N_2 at 18° and 754 mm.
Calc. for $C_{16}H_{13}NS$: N, 5.6. Found: N, 5.5.

Properties of Phenylpropiolthio-*p*-toluid.—It is readily soluble in alcohol, ether, chloroform, etc. It is decomposed somewhat by boiling with solvents, so is best purified by evaporating an alcohol or ether solution to a small bulk at room temperature. Fine, shining, yellow needles separate out which melt with decomposition at 111–113°. The toluid is only very slightly soluble in sodium or potassium hydroxide solution.

Sodium Salt of Phenylpropiolthio-*p*-toluid, $C_6H_5C \equiv CCSNa.NC_6H_4CH_3$.—This was formed by the interaction of sodium phenylacetylene and *p*-tolyl mustard oil as already described, the substance separating from the ether in little balls of colorless microscopic needles. It is unstable in water, reacting immediately to form sodium hydroxide and phenylpropiolthiotoluid.

Bi-phenylpropiolthio-*p*-toluid, $(C_6H_5C \equiv CCSNHC_6H_4CH_3)_2$.—An ether solution of the thiotoluid containing a few drops of aqueous sodium hydroxide was heated to boiling. The solution became dark red in color and in a few minutes the sides of the tube were coated with brilliant reddish brown crystals. The substance in an amorphous condition was also prepared by boiling the thiotoluid with aqueous potassium hydroxide. The resulting dark colored mass was purified by crystallization from benzene. The crystals were filtered, washed with dilute alcohol and dried at 100°.

0.12 subst. gave 5.9 cc. N_2 at 18° and 761 mm.
Calc. for $(C_{16}H_{13}NS)_2$: N, 5.6. Found: N, 5.8.

The new compound was obviously a polymer of phenylpropiolthio-*p*-toluid and was considered to be bi-molecular.

Properties of Bi-phenylpropiolthio-*p*-toluid.—It is only slightly soluble in alcohol, ether and ligroin, but moderately soluble in chloroform and benzene. It is best recrystallized by dissolving in the warm solvent and then evaporating to a small bulk. It crystallizes from benzene in small narrow plates which are garnet red when viewed through the microscope. No definite melting point of the polymerized thiotoluid was observed. The crystals gradually soften and merge together when heated above 200°, but are not melted at 260°.

Action of Phenylhydrazine on Phenylpropiolthio-*p*-toluid.—Two grams of the substance dissolved in alcohol were mixed with the molecular equivalent of the base and refluxed for several hours on a water bath or until there was no further evolution of hydrogen sulfide. The brick red precipitate which collected on cooling was filtered and dried. This apparently contained some polymerized thiotoluid mixed with considerable tarry material from which no crystalline compound could be isolated.

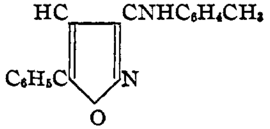
Action of Hydroxylamine on Phenylpropiolthio-*p*-toluid.—A small excess over the molecular amount of the free hydroxylamine base in alcohol solution[1] was added to two grams of the thiotoluid dissolved in several volumes of alcohol and refluxed for three hours on a water bath. A yellow crystalline mass separated out on cooling. This was recrystallized several times from alcohol diluted with water. It was finally filtered, washed with dilute alcohol and dried at 100°. The yield was very poor.

0.1 g. subst. gave 10.0 cc. N_2 at 13° and 748 mm.

Calc. for $C_{16}H_{14}ON_2$: N, 11.4. Found: N, 11.6.

The new compound is 3-*p*-toluidino-5-phenylisoxazol, the first formed oxime rearranging to the cyclic form.

$C_6H_5C \equiv CCNOH.NHC_6H_4CH_3 =$



Properties of *p*-Toluidinophenylisoxazol.—It is readily soluble in alcohol, ether, benzene and glacial acetic acid. It crystallizes from alcohol in lustrous, white, six-sided plates, which melt sharply at 141.5°. It is stable toward acids and is unchanged by prolonged boiling with hydrochloric acid.

Phenylpropiolthio-*m*-toluid, $C_6H_5C \equiv CCSNHC_6H_4CH_3$.—Three grams of *m*-tolyl mustard oil were added to the molecular equivalent of sodium phenylacetylene suspended in ether and kept at room temperature for twenty-four hours. No apparent change took place, except for the development of an orange color. It was refluxed for several hours,

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[1] Volhard, *Ann.*, 253, 224 (1889).

then the ether was partially driven off, replaced with benzene and the mixture again refluxed for two hours. The mixture was poured into water, the water layer separated and cooled with ice. Cold dilute hydrochloric acid was added slowly with stirring. A yellow, crystalline precipitate formed in a few minutes. This was filtered, washed several times with a little ether and dried in vacuum. The yield was poor and only about a gram of the new toluid was obtained.

0.2 g. subst. gave 10.0 cc. N_2 at 20° and 756 mm.
Calc. for $C_{16}H_{13}NS$: N, 5.6. Found: N, 5.8.

Properties of Phenylpropiolthio-*m*-toluid.—It is soluble in alcohol, ether, benzene, etc. It crystallizes from alcohol in fine, slender, yellow needles. It is best purified by digestion with small portions of warm ether in which it is only slightly soluble. It melts with decomposition at 118–120°. It is readily soluble in sodium hydroxide solution from which it is precipitated by the addition of an excess of acid. No polymerized form was observed. When heated with aqueous or alcoholic sodium hydroxide it changes into a tar. The amount of thiotoluid was insufficient to permit an investigation of the action of phenylhydrazine and hydroxylamine, although small test tube experiments indicated that a reaction takes place in each case with the elimination of hydrogen sulfide.

The Action of *o*-Tolyl Mustard Oil on Sodiumphenylacetylene.—Two grams of phenylacetylene were converted into the sodium derivative, in ether, and the molecular equivalent of *o*-tolyl mustard oil added. No apparent change took place, so the mixture was refluxed for eight hours. It was then poured into water and the two layers separated. The water extract was cooled with ice and acidified in the usual manner. A small amount of a dark-colored oil separated out. It did not solidify on standing and was not further examined. The ether extract in addition to considerable unchanged mustard oil and phenylacetylene contained a small amount of a substance which separated on the sides of the beaker in shining nearly colorless plates. This crystalline mass proved to be a sodium derivative, soluble in water, which on the addition of acid reprecipitated as an oil.

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THE IDENTIFICATION OF ACIDS. II.

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In a recent article[1] it was shown that the *p*-nitrobenzyl esters of many acids are readily prepared and have properties which render

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[1] THIS JOURNAL, 39, 124 (1917).