clearly under the microscope. Both forms are colorless and melt at 210° (corr.).

Subst. (I) 0.1705, (II) 0.1000; cc. 0.1 *N* $AgNO_3$. (I) 16.87, (II) 9.88.
Calc. for $C_{15}H_5O_4NCl_4$: Cl, 35.02%. Found: (I) 35.08, (II) 35.04.

Tetrachlorophthalyl Phenyl Hydrazone.—5.0 g. of tetrachlorophthalic anhydride in 200 cc. glacial acetic acid were added to 2 cc. of phenylhydrazine in 25 cc. of the same solvent and the mixture boiled for 15 minutes. The first reaction is the formation of anilino-tetrachloro-phthalamic acid, but this readily splits off a molecule of water during the heating and gives orange needles of the phenylhydrazone. The product was recrystallized from glacial acetic acid and from alcohol. The yellow plate modification was obtained by very rapid cooling of an acetic acid solution. It is unstable and rapidly reverts to the orange needles. The substance melts at 287° (corr.).

Subst. (I) 0.0793, (II) 0.0977; cc. 0.1 *N* $AgNO_3$. (I) 8.23, (II) 10.37.
Calc. for $C_{14}H_6O_2N_2Cl_4$: Cl, 37.73%. Found: (I) 37.75, (II) 37.64.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES: CONSTITUTION AND COLOR.

XIII.[1] TETRAIODOPHTHALOXIME AND SOME OF ITS DERIVATIVES.

BY DAVID S. PRATT AND THOMAS B. DOWNEY.

Received November 16, 1917.

The large proportion of iodine in tetraiodophthalic anhydride and its sulfur yellow color, probably due to the proximity effects of the unsaturated halogen atoms, made it desirable to prepare the corresponding oxime. The study of substituted phthalic acid compounds was, therefore, made to include the material reported in this paper. Tetraiodophthalic anhydride represents the maximum molecular weight possible in a halogenated ring, the presence of the most unsaturated halogen atoms, and the greatest effect obtainable by this type of substitution.

Tetraiodophthaloxime was obtained without difficulty. 50.0 g. of tetraiodophthalic anhydride,[2] ground to a fine powder, were added to a solution of 6.4 g. hydroxylamine sulfate and 6.6 g. sodium bicarbonate in 250 cc. water. The suspension was warmed in a boiling water bath for 2 hours with occasional stirring, finally acidified with hydrochloric acid to break up any oxime salt, and filtered. The product was washed thoroughly with hot water until free from inorganic matter and dried. Yield, 52.0 g. crude oxime or 93% theoretical.

The impure product was recrystallized until pure from glacial acetic

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[1] THIS JOURNAL, 40, 407 (1918).

[2] Pratt and Shupp, *Ibid.*, 40, 254 (1918).

acid and obtained as long, lemon yellow needles which decompose without melting. It is slightly soluble in hot acetic acid, less in alcohol and other organic solvents. No other form was obtained, although many attempts were made under a variety of conditions.[1] Iodine was determined by the lime combustion method.

Subst. (I) 0.4345, (II) 0.4638; cc. 0.1 *N* $AgNO_3$. (I) 26.10, (II) 27.84.
Calc. for $C_8HO_3NI_4$: I, 76.14%. Found: (I) 76.23, (II) 76.18.

The very marked yellow color of the anhydride itself makes it probable, if not certain, that the modification of this oxime corresponding to the colorless phthaloxime would be yellow. The more highly colored form analogous to yellow phthaloxime would then be yellow or orange. It could not be determined, therefore, which of the two possible modifications were obtained. The slight solubility of tetraiodophthaloxime in all solvents may have been responsible for the non-appearance of a pseudomorphic modification.

The salts of tetraiodophthaloxime are red in color, and are insoluble in all solvents. Aqueous ammonia precipitated its salt from an alcoholic solution of the oxime, but it lost ammonia on drying. A weighed sample of oxime in a porcelain boat was exposed to dry ammonia gas for 2 weeks without gain in weight or change in color. This is remarkable as unhalogenated phthaloxime readily absorbs one molecule of ammonia giving the salt, and the iodine derivative would be expected to show stronger acidic properties.

Silver Salt.—The silver salt was made by adding a hot solution of silver nitrate in just enough ammonium hydroxide to redissolve the oxide to a hot alcoholic solution of tetraiodophthaloxime. The salt precipitated at once in red, flocculent form. It was filtered off, washed free from excess silver and dried at 100°. Analysis was made by treating with dilute nitric acid and titrating with standard ammonium thiocyanate.

Subst. (I) 0.2325, (II) 0.2933; cc. 0.1 *N* NH_4SCN. (I) 2.60, (II) 3.33.
Calc. for $C_8O_3NI_4Ag$: Ag, 13.95%. Found: (I) 12.07, (II) 12.18.

Methyl Ether.—The methyl ether was prepared by suspending 10 g. of dry silver salt in 100 cc. ethyl ether containing 5 cc. methyl iodide. The reaction proceeded slowly at room temperature and was complete within 24 hours. The mixture of silver iodide and methyl ether was filtered off and extracted with 4 liters of boiling glacial acetic acid. 6 g. of canary yellow needles were obtained representing a yield of 70 per cent. The ether does not melt.

Subst. (I) 0.5352, (II) 0.3608; cc. 0.1 *N* $AgNO_3$. (I) 30.87, (II) 21.22.
Calc. for $C_9H_3O_3NI_4$: I, 74.58%. Found: (I) 73.21, (II) 74.65.

Ethyl Ether.—The ethyl ether was made similarly. A yield of 60%

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[1] See Pratt and Miller, THIS JOURNAL, **40**, 407 (1918).

theoretical was obtained as lemon yellow needles without melting point. No other form was observed.

Subst. (I) 0.3176, (II) 0.3782; cc. 0.1 *N* $AgNO_3$. (I) 18.30, (II) 21.83.
Calc. for $C_{10}H_5O_3NI_4$: I, 73.06%. Found: (I) 73.13, (II) 73.26.

Normal Propyl Ether.—5 g. of silver salt, 8 cc. normal propyl bromide and 30 cc. ether were placed in a small pressure flask and heated to 100° for 4 hours, during which time the color gradually changed to a dirty yellow. The mixture was filtered off and extracted with 500 cc. boiling acetic acid. Yield, 4 g. or 90% theoretical. The ether was obtained as lemon yellow needles without melting point. It decomposed readily on heating.

Subst. (I) 0.2269, (II) 0.2098; cc. 0.1 *N* $AgNO_3$. (I) 12.83, (II) 11.83.
Calc. for $C_{11}H_7O_3NI_4$: I, 71.62%. Found: (I) 71.77, (II) 71.57.

Isopropyl Ether.—This was prepared similarly to the above in 82% yield. The ether gave yellow needles which did not melt.

Subst. (I) 0.1828, (II) 0.0889, cc. 0.1 *N* $AgNO_3$. (I) 10.33, (II) 5.02.
Calc. for $C_{11}H_7O_3NI_4$: I, 71.62%. Found: (I) 71.72, (II) 71.66.

Normal Butyl Ether.—Silver salt suspended in ether reacted readily with normal butyl iodide at room temperature to give a 90% yield of the ether in the form of light yellow needles without melting point.

Subst. (I) 0.3394, (II) 0.2919; cc. 0.1 *N* $AgNO_3$. (I) 18.63, (II) 16.23.
Calc. for $C_{12}H_9O_3NI_4$: I, 70.24%. Found: (I) 69.67, (II) 70.42.

Isoamyl Ether.—The isoamyl ether decomposed more readily than the preceding derivatives. It was obtained from silver salt suspended in ether and isoamyl iodide, at room temperature for 20 hours. The ether was extracted from the residue by acetic acid as yellow needles without melting point. Yield, 75%.

Subst. (I) 0.1743, (II) 0.1063; cc. 0.1 *N* $AgNO_3$. (I) 9.50, (II) 5.78.
Calc. for $C_{13}H_{11}O_3NI_4$: I, 68.90%. Found, (I) 69.18, (II) 69.01.

Normal Octyl Ether.—This was made from silver salt and normal octyl iodide in the usual way. It was recrystallized from acetic acid, avoiding long heating, and dried below 100°. The ether forms yellow needles which do not melt.

Subst. (I) 0.2944, (II) 0.3061; cc. 0.1 *N* $AgNO_3$. (I) 15.09, (II) 15.49.
Calc. for $C_{16}H_{17}O_3NI_4$: I, 65.03%. Found: (I) 65.05, (II) 64.23.

Allyl Ether.—The allyl ether from silver salt and allyl iodide gave light yellow crystals in 90% yield. No melting point.

Subst. (I) 0.1148, (II) 0.1328; cc. 0.1 *N* $AgNO_3$. (I) 6.47, (II) 7.51.
Calc. for $C_{11}H_5O_3NI_4$: I, 71.82%. Found: (I) 71.54, (II) 71.74.

Benzyl Ether.—10 g. silver salt and 35 cc. benzyl chloride were heated 2–3 hours on a water bath, during which the color changed to a dirty brown. The precipitate was filtered off and extracted with 2.5 liters of boiling acetic acid. The benzyl ether crystallized out on cooling as long, yellow needles without melting point. Yield, 65%.

Subst. (I) 0.1653, (II) 0.1832; cc. 0.1 N $AgNO_3$. (I) 8.74, (II) 9.67.
Calc. for $C_{15}H_7O_3NI_4$: I, 67.08%. Found: (I) 67.11, (II) 66.99.

Acetate.—5 g. of pure tetraiodophthaloxime were dissolved in 75 cc. acetic anhydride by heating below the boiling point for about 40 minutes. The acetate crystallized out on cooling in bright yellow needles. It was purified from ethyl acetate.

Subst. (I) 0.2043, (II) 0.1699; cc. 0.1 N $AgNO_3$. (I) 11.52, (II) 9.59.
Calc. for $C_{10}H_3O_4NI_4$: I, 71.62%. Found: (I) 71.60, (II) 71.62.

Benzoate.—8 g. of pure tetraiodophthaloxime were dissolved in 65 cc. of benzoyl chloride 135–150°, and heated at this temperature for 30 minutes. The benzoate was precipitated by adding alcohol, filtered, and washed free from ethyl benzoate. The yellow needles showed no melting point.

Subst. (I) 0.5980, (II) 0.6311; cc. 0.1 N $AgNO_3$. (I) 31.06, (II) 32.61.
Calc. for $C_{15}H_5O_4NI_4$: I, 65.86%. Found: (I) 65.92, (II) 65.59.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE.]

ON THE ADDITION OF SODIUM ACETOACETIC ESTER TO THE AROMATIC MUSTARD OILS.

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Received November 16, 1917.

Introduction.

In the course of an investigation of the action of phenylhydrazine and hydroxylamine on thio derivatives it became necessary to prepare the monothioanilide of acetomalonic ester, $CH_3COCH(CSNHC_6H_5)COOC_2H_5$. No experimental details were found for the preparation of this ester and since few compounds of this type have been made, a short study was made of their synthesis and reactions.

Michael[1] first pointed out that thioanilides may be built up, through the sodium derivative, by the action of sodium malonic ester on the mustard oils. With phenyl mustard oil the reactions were expressed as follows:

$$CHNa(COOC_2H_5)_2 + C_6H_5NCS = CH(CSNa.NC_6H_5)(COOC_2H_5)_2$$

$$CH(CSNa.NC_6H_5)(COOC_2H_5)_2 + \text{acid} \longrightarrow CH(CSNHC_6H_5)(COOC_2H_5)_2$$

A similar reaction would be expected with any ester containing an acidic methylene group. Thus Ruheman[2] found that sodium cyanomalonic ester as well as sodium malonic ester added to phenyl mustard oil forming thioanilides. Sodium acetoacetic ester[3] also reacts with phenyl mustard oil.

[1] *J. prakt. Chem.*, [2] **35**, 450 (1887).

[2] *J. Chem. Soc.*, **93**, 621 (1908).

[3] Michael, *J. prakt. Chem.*, [2] **60**, 286 (1899).