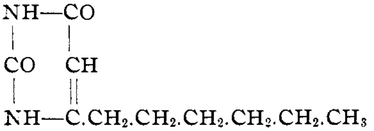
hydrochloric acid. The crude pyrimidine melted at 140–141° and the yield was about 4.5 g.

Desulfurization of 2-Thio-4-hexyluracil with Formation of 4-hexyluracil,



—The best conditions for the successful conversion of the 2-thiopyrimidine into this pyrimidine are as follows: Equal parts by weight of the thiopyrimidine and monochloroacetic acid are dissolved in about 12–13 times their combined weight of water (4 g. of pyrimidine to 100 cc. of water). While the chloroacetic acid dissolves immediately at ordinary temperature it is necessary to boil for several minutes before solution of the pyrimidine is effected. After complete solution of the pyrimidine, the mixture is then boiled for several hours. After solution of the pyrimidine it is best to add about 10 cc. of dilute hydrochloric acid to aid the reaction. After digesting for about 7–8 hours (working with 4 g. of pyrimidine) the reaction is complete, and, on cooling the solution, hexyluracil separates as an oil which soon solidifies. This pyrimidine is extremely insoluble in boiling water and separates on cooling in beautiful, glistening plates which melt at 170° to a clear oil without effervescence. The yield is practically quantitative. The pyrimidine did not lose weight when heated at 110–120°, and did not respond to a test for sulfur. Nitrogen determination:

Calc. for $C_{10}H_{16}O_2N$: N, 14.28; found: N, 14.15.

This pyrimidine is extremely soluble in alcohol and separates in plates when an alcoholic solution is diluted with water. It dissolves also in sodium hydroxide solution.

NEW HAVEN, CONN.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE ACTION OF NITRIC ACID ON IODOANIL.

BY LATHAM CLARKE AND E. K. BOLTON.[1]

Received July 10, 1914.

Owing to the absence from the country of both the authors it has been necessary for me to prepare this work for publication.—C. L. JACKSON.

The object of the work described in this paper was to compare the behavior of iodoanil and chloroanil with nitric acid. Stenhouse[2] obtained from the latter chloropicrine and oxalic acid. As he found that chloroanilic acid behaved in the same way, and that bromoanilic acid gave bromo-

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Elmer Keiser Bolton.

[2] *J. Chem. Soc.*, 8, 6 (1870).

picrine and oxalic acid, it is probable that bromoanil would undergo a similar reaction; but our experiments show that the action with iodoanil is entirely different, since nitric acid converts it into iodine pentoxide and diiodomaleic acid; and this difference is due to the nature of the substances, not to a less energetic action in our experiments than in those of Stenhouse, since we used fuming nitric acid instead of the strong acid used by him, and heated the mixture on the steam bath from 4 to 5 hrs., followed, after the removal of the iodine pentoxide, by evaporation of the acid from 300 to 50 cc. Therefore, if the diiodomaleic acid were only an intermediate stage in the formation of iodopicrine and oxalic acid, we must have obtained some of these products, but the most careful search revealed no trace of them.

The identification of the diiodomaleic acid was not an easy matter. We could find no method of purifying it in spite of many and varied attempts, and the analyses gave bad results, which were explained in part by the formation of the anhydride, as we found that this substance was formed by long standing *in vacuo*; but only in part, since the anhydride gave equally bad analytical results, and also melted 4° lower than the specimen prepared by Diels and Reinbeck.[1] It seems, therefore, that both our acid and anhydride contained some clinging impurity, which we could not remove by crystallization. The composition of our two substances was, however, established by determinations of the molecular weight of the anhydride, and analyses of the sodium salt and aniline salt of the acid, of several of its other derivatives, and by titrations, which showed that it was dibasic. Three different compounds agree with these results, diiodosuccinic acid, diiodomaleic acid, and diiodofumaric acid. The last of these can be rejected at once, since our acid forms an anhydride easily. For instance, on heating the acid with toluene, in which it is insoluble, it gradually went into solution, while at the same time a drop of water appeared in the toluene, and upon evaporating the solvent, the anhydride already mentioned was obtained. The decision between the maleic and succinic acid was more difficult. Our compound did not act with bromine, but this has no weight, as it has been shown[2] that the presence of a halogen frequently interferes with the addition of bromine to an unsaturated acid. The potassium permanganate test for a double bond could not be applied, since it decomposed our acid with liberation of iodine—a behavior frequently observed even with saturated iodine compounds; reducing agents also gave no definite results with it, so that it was impossible to settle the question by experiment. In spite of this, however, it seems to us that the following considerations exclude diiodosuccinic acid: To form this com-

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[1] *Ber.*, **43**, 1271 (1910).

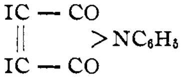
[2] Bauer, *Ber.*, **37**, 3317 (1904); Pum, *Monats.*, **9**, 449 (1888).

pound from iodoanil it would be necessary to add two atoms of hydrogen to that substance, which would obviously be impossible in the presence of hot, fuming nitric acid. The diiodosuccinic acid has not as yet been prepared, and it may be doubted whether it is stable enough to exist, as Finkelstein[1] obtained by the action of sodium iodide on dibromosuccinic acid in acetone solution, sodium bromide, iodine, and fumaric acid, and Brunner and Chuard[2] found the same products on treating monobromosuccinic acid with potassium iodide in alcohol. Our somewhat impure diiodomaleic anhydride melts 4° below the pure compound made by Diels and Reinbeck,[3] but at least 20° higher than the known dihalogen succinic anhydrides.

On the other hand, our anhydride differs from that described by Diels and Reinbeck in two particulars besides the melting point. They state it is yellow and insoluble in benzene, whereas we found it white, turning yellow on exposure to air, and soluble in benzene, in sharp contrast to the insolubility of the diiodomaleic acid. Skraup[4] has found that maleic acid is converted into fumaric acid by heating it with strong nitric acid, but, although our acid was submitted to the long-continued action of hot, fuming nitric acid, we obtained only maleic acid, (shown by its easy conversion into an anhydride); it seems, therefore, that the presence of the two atoms of iodine in our acid must prevent this transformation.

So far as we can find, this is the first time that maleic acid has been formed from a substituted quinone by nitric acid, but the reaction has been brought about by other reagents.[5]

If the acid aniline diiodomaleate is suspended in glacial acetic acid, and heated, it is converted into the diiodomaleylphenylimide (or anil), which must have the ring formula given below. It melts at 171–172° (uncor.).



$$\begin{array}{l} \mathrm{IC-CO} \\ \| \qquad\quad >\mathrm{NC_6H_5} \\ \mathrm{IC-CO} \end{array}$$

By the further action of aniline in alcoholic solution, this substance is converted into the phenylaminomaleylphenylimide (anilinomaleylanil), melting at 232–233° (uncor.), which has been made frequently before, and found to melt at 230°,[6] 231°,[7] 232–233°,[8] or 235°.[9] Dichloro- or dibromomaleic acid, when treated with aniline, retains one atom of halo-

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[1] *Ber.*, **43**, 1528 (1910).

[2] *Ibid.*, **30**, 200 (1897).

[3] *Ibid.*, **43**, 1271 (1910).

[4] *Monats.*, **11**, 323 (1890); **12**, 124 (1891).

[5] Zincke, Fuchs, *Ann.*, **267**, 1 (1892); Kempf, *Ber.*, **39**, 3715 (1906).

[6] Michael, *Ber.*, **19**, 1377 (1886).

[7] Reissert, Tiemann, *Ber.*, **19**, 622 (1886); Reissert, *Ibid.*, 1644 (1886).

[8] Wohl, Freund, *Ber.*, **40**, 2300 (1907).

[9] Bischoff, Walden, *Ann.*, **279**, 140 (1894).

gen,[1] which is in harmony with the observation frequently made in this laboratory that iodine is replaced by hydrogen more easily than bromine, bromine than chlorine.

p-Toluidine gave with diiodomaleic acid *p*-tolylaminomaleyl-*p*-tolylimide, which we found to melt at 229° (uncor.). Junghahn and Reissert[2] found 228°. Phenylhydrazine gave, with diiodomaleic acid, as the principal product diiodomaleylphenylhydrazide melting at 170° (uncor.) and in smaller quantity a substance melting at 266–267° (uncor.), which we suppose to be phenylhydrazomaleylphenylhydrazide, but did not obtain enough of it to settle its composition.

When the diiodomaleic acid was heated with water to 100° in a sealed tube, we obtained carbon dioxide, formaldehyde, hydriodic acid, and a little free iodine, and in addition to these soluble compounds a brown oil, solidifying on standing, from which two white solids were obtained. One gave a percentage of iodine agreeing with that for diiodoacetic acid, but as it was white, and melted at 95–96° (uncor.), we cannot consider its nature settled, since diiodoacetic acid is pale yellow, and melts at 110°.[3] Unfortunately, this work was begun so late in the year that we had not time enough to find the explanation of this discrepancy. For the same reason we, can give only a preliminary account of the second substance, melting at 182–184° (uncor.). A single determination of iodine indicates that it is the as yet undiscovered pentaiodoethane.

Experimental.

Action of Fuming Nitric Acid on Iodoanil.—Thirty-five grams of crude iodoanil were mixed with 300 cc. of nitric acid of specific gravity 1.50, and heated on a sand bath to slow boiling in a flask fitted by a ground joint to an air return condenser. After half an hour a white solid separated, which increased in amount, as the reaction continued. At the end of 4 or 5 hrs., after the brown color of the iodoanil had disappeared, the orange-red acid solution was allowed to cool, and decanted from the white solid, which was washed with a little strong nitric acid, the washings being added to the main portion of the acid. This white solid showed the properties of iodine pentoxide, as it sublimed at about 300° with partial decomposition into iodine and oxygen, but gave off no water; absorbed moisture from the air changed its cream color to the pure white of iodic acid; and its strongly acid aqueous solution set free chlorine from hydrochloric acid, or iodine from potassium iodide. It was prepared for analysis by washing with glacial acetic acid, drying *in vacuo* over potassium hydroxide, and finally washing with benzene and drying *in vacuo*.

Calc. for I_2O_5: I, 76.04; found: I, 76.00, 75.90.

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[1] Michael, *Am. Chem. J.*, **9**, 180 (1867); Anschütz, Beavis, *Ann.*, **295**, 29 (1897); Salmony, Simonis, *Ber.*, **38**, 2580 (1905).

[2] *Ber.*, **24**, 1766 (1891).

[3] Angeli, *Ber.*, **26**, 596 (1893).

35 g. of the iodoanil gave 26 g. of iodine pentoxide.

For further identification the aniline iodate was made by adding a mixture of aniline and alcohol to an aqueous solution of the acid. The precipitate formed was washed with alcohol and benzene.

Calc. for $C_6H_5NH_2HIO_3$: I, 47.18; found: I, 47.87.

The analysis was attended with difficulty, because the salt explodes violently, when brought in contact with nitric acid, so that only one of the Carius tubes used by us escaped being blown to pieces. Our observations confirm the properties of the salt as given by Beamer and F. W. Clarke,[1] the explosiveness with nitric acid, and the fact that the crystals turn blue on exposure to the air being the only points we have to add to their description.

Diiodomaleic Acid.—The orange-red acid solution poured off from the iodine pentoxide was evaporated on the steam bath until reduced to about 50 cc., when it was freed from any additional iodine pentoxide by decantation, or if necessary, filtration through glass wool covered with a thin layer of asbestos, and allowed to cool. Rosets of long, white needles separated, which were filtered out on a fine Büchner filter and freed from adhering acid by a porous plate and standing in a desiccator over potassium hydroxide. A second crop of crystals was obtained by evaporating the filtrate to 25 cc., but further evaporation yielded only a small additional amount contaminated with iodine pentoxide. No test for oxalic acid was obtained from the solution. From 35 g. of iodoanil 11 g. of the crystals were obtained, or 52% of the theoretical yield, if one molecule of the product was obtained from each molecule of iodoanil. This product was recognized as diiodomaleic acid by analyses of some of its derivatives given later. No good analyses of the acid itself could be obtained, the percentages of iodine and of carbon coming out somewhat over 1% too high for the theory. This was in part due to formation of anhydride during the drying *in vacuo*, as a specimen which stood *in vacuo* for one week showed an increase of 0.8% in its iodine, but this was not the only reason, as our analyses of the anhydride were even worse, coming out not far from 2% too high on both the iodine and carbon. We have not found any method for the purification of the diiodomaleic acid, as no good results could be obtained from crystallizations even from mixed solvents, or precipitations from its solutions, and once dissolved it could be recovered only by evaporation to dryness. Benzene with alcohol, and acetone with chloroform were tried with especial care, other combinations less thoroughly. Strong sulfuric acid precipitated the compound from its aqueous solution, but failed to purify it; strong hydrochloric acid did not even precipitate it. The acid formed by the action of water on the

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[1] *Ber.*, 12, 1066 (1879).

anhydride gave no better results on analysis than the acid as formed direct from nitric acid.

Properties of Diiodomaleic Acid, $C_2I_2(COOH)_2$.—It crystallizes from fuming nitric acid in rosets of long, white needles. Our best specimens melted at 142° with evolution of bubbles, and the formation of a pale yellow liquid, but the true melting point is undoubtedly higher, as the analyses showed that our substance was not pure, containing the anhydride undoubtedly, and probably a second impurity. It is very soluble in water, methyl or ethyl alcohol, ether, acetone, glacial acetic acid, acetic ester, or nitrobenzene; insoluble in chloroform, carbon tetrachloride, carbon disulfide, benzene, toluene, or naphtha. No good solvent could be found for it. Boiling benzene, or toluene, converts it into the anhydride, which dissolves as it forms. The acid is less soluble in sulfuric acid than in water.

The aqueous solution of the diiodomaleic acid gave an acid reaction with litmus and decomposed carbonates with effervescence. A specimen crystallized from the nitric acid was dried on a porous plate and then *in vacuo* over potassium hydroxide, and washed several times with warm benzene, after which it was titrated with a 0.2 *N* potassium hydroxide solution, using phenolphthalein as the indicator.

Subst. I, 1.1120, 0.540 g.; II, 0.847, 0.764 g.; KOH, 0.373, 0.180, 0.285, 0.257. Number of carboxyl groups, 2.1, 2.1, 2.1, 2.1.

The acid is therefore dibasic. II was a specimen prepared from the anhydride with water.

Sodium Diiodomaleate, $C_2I_2(CO_2Na)_2$.—Three grams of diiodomaleic acid, dissolved in 50 cc. of absolute alcohol, were treated with sodium ethylate[1] as long as a precipitate was formed. The salt was washed six times with alcohol and dried *in vacuo.*

Subst. 0.5856, 0.7417 g.; Na_2SO_4, 0.2080, 0.2645 g.; calc. for $C_2I_2(CO_2Na)_2$: Na, 11.16; found: Na, 11.50, 11.55.

It forms small, white plates soluble in water but insoluble in all the common organic solvents.

An aqueous solution of the diiodomaleic acid gave a white precipitate with silver nitrate, which exploded violently when heated in an air bath. A solution of the ammonium salt gave a white precipitate with lead acetate, but no action with a salt of calcium, strontium or barium.

When a solution of diiodomaleic acid in either water or alcohol was treated with a drop of bromine water, no decoloration was observed. An aqueous solution of the acid decolorized potassium permanganate with precipitation of manganese dioxide, but nothing definite could be isolated from the product. Diiodomaleic acid was dissolved in alcohol and saturated with hydrochloric acid gas, the product was a brown liquid, which

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[1] Salmony, Simonis, *Ber.*, **38**, 2580 (1905).

could not be made to solidify, and was not studied further. Attempts to reduce the acid with sodium amalgam with water or alcohol, zinc or magnesium and sulfuric acid, or zinc dust and acetic acid, gave no results from which a definite compound could be isolated.

Diiodomaleic Anhydride.—Five grams of diiodomaleic acid were heated in 50 cc. of toluene until the solid had gone into solution. A few drops of a liquid separated, which was shown to be water by its action with dried copper sulfate. The yellow anhydride, obtained by evaporating off the solvent, after several crystallizations from naphtha, showed the constant m. p. 112–112.5° (uncor.), but analyses gave 1.5% to 1.9% too much iodine, and 1.5% to 1.4% too much carbon. A specimen of the anhydride, prepared by the action of acetyl chloride and a drop of sulfuric acid on the acid, gave 1.1% too much iodine, and after two more crystallizations, making 8 in all, 1.2% too much. It is evident, therefore, that our diiodo acid and anhydride contain a clinging impurity, which cannot be removed by crystallization, and this is confirmed by the fact that the constant melting point of our diiodomaleic anhydride, 112–112.5° (uncor.) is 4° below that obtained by Diels and Reinbeck,[1] who made this substance by the action of sodium iodide on dibromomaleic anhydride in dry acetone. The properties of our substance are identical with those given by Diels and Reinbeck except that our preparation crystallizes in white prisms, which soon turn light yellow, while they describe theirs as yellow, and ours is soluble in benzene, theirs difficultly soluble. Although our analyses gave no satisfactory results, we were more successful with the determination of the molecular weight by freezing in benzene.

Calc. for $C_2I_2(CO)_2O$: 350; found: 312.5, 322.7, 316.6, 320.9.

The anhydride is converted into the acid slowly by cold, quickly by hot water. That our substance was the diiodomaleic anhydride is proved, in spite of our bad results on the substance itself, by the analyses of its derivatives already given and by those that follow.

Acid Aniline Salt of Diiodomaleic Acid, $C_2I_2COOHCOOHNH_2C_6H_5$.—Two grams of diiodomaleic acid, dissolved in 150 cc. of ether, were treated with 4 cc. of aniline, and the white precipitate, after purification by washing with ether, was dried *in vacuo.*

Calc. for $C_2I_2COOHCOOHNH_2C_6H_5$: I, 55.07; found: I, 55.33, 55.58.

It decomposes at about 152°, is soluble in water but insoluble in most of the common organic solvents. Its solution has an acid reaction to litmus, and is decomposed by sodium hydroxide with an odor of aniline. It is also decomposed if heated in an organic solvent.

Diiodomaleylphenylimide (Diiodomaleylanil), $C_2I_2(CO)_2NC_6H_5$.—The acid aniline diiodomaleate, described above, was made by adding a slight ex-

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[1] *Ber.*, **43**, 1271 (1910).

cess of aniline to a solution of diiodomaleic acid in glacial acetic acid. The precipitate of the salt, which formed in a few minutes after being washed free from aniline with glacial acetic acid, was suspended in glacial acetic acid and heated on the sand bath, until it began to dissolve, when the lamp was removed and the flask allowed to stand on the hot sand till the solution was complete. The addition of a small quantity of water then threw down a yellow precipitate, which was crystallized from alcohol until it showed the constant m. p. 171–2° (uncor.).

Subst. 0.2502; AgI, 0.2758; Calc. for $C_2I_2(CO)_2NC_6H_5$: I, 59.74; found: I, 59.58.

Properties of Diiodomaleylphenylimide.—Small, yellow prisms melting at 171–172° (uncor.); soluble in ether, chloroform, acetone, ethyl acetate, glacial acetic acid, benzene, toluene, nitrobenzene, or aniline; essentially insoluble in cold alcohol, or naphtha, soluble when hot. Strong hydrochloric acid produces no visible effect on it, even when hot; boiling alkali dissolves it slowly.

Further action of aniline converted the diiodo compound into phenylaminomaleylphenylimide[1] (anilinomaleylanil), which was also obtained when diiodomaleic acid was dissolved in alcohol, and treated with aniline in the proportion of 3 molecules to 1 of the acid; the mixture, disregarding the precipitate of the salt, was heated on the steam bath, which turned the liquid brown, and produced vapors of iodine. At the end of an hour the solution was allowed to cool, and the yellow product which separated was washed with cold alcohol and then crystallized from alcohol and later from benzene or toluene till it showed the m. p. 232–233° (uncor.).

Calc. for $C_6H_5NHC_2H(CO)_2NC_6H_5$: C, 72.69; H, 4.58; N, 10.61; found: C, 72.24; H, 4.54; N, 10.48.

The substance can be prepared as well in a glacial acetic acid solution and is even formed when water is the solvent. Diiodomaleic anhydride also gave it when heated with aniline in absolute alcohol or glacial acetic acid.

In preparing the imide, occasionally a different product was obtained in small, yellow needles, melting at 261° (uncor.). It seemed to be phenylaminoiodomaleylphenylimide, but we did not have time to study it.

If the diiodomaleic acid was heated with *p*-toluidine and glacial acetic acid, the *p*-tolylaminomaleyl-*p*-tolylimide was formed, which was crystallized from alcohol till it melted constant at 229° (uncor.).

Calc. for $C_7H_7NHC_2H(CO)_2NC_7H_7$: N, 9.59; found: N, 9.37.

Action of Phenylhydrazine on Diiodomaleic Acid.—Three grams of diiodomaleic acid, dissolved in 50% alcohol, were treated with phenylhydra-

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[1] Reissert, Tiemann, *Ber.*, **19**, 622; Reissert, *Ibid.*, p. 1644 (1886); Michael, *Ibid.*, p. 1377; Wohl, Freund, *Ber.*, 40, 2300 (1907); Bischoff, Walden, *Ann.*, **279**, 140 (1894).

zine in the proportion of 3 molecules to 1. After heating for 5 minutes on the steam bath, red needles separated, which were filtered out of the hot solution. The filtrate, on cooling, deposited a few orange crystals, which were obtained in quantity by adding a little water to the solution. This is the principal product of the reaction, and it was purified by crystallization from 50% alcohol till it showed the constant m. p. 170° (uncor.), when it was dried *in vacuo.*

Subst. 0.3172, 0.2262; N_2, 18 cc. at 21° and 766 mm.; AgI, 0.2393; Calc. for $C_2I_2(CO)_2NNHC_6H_6$: N, 6.37; I, 57.70; found: N, 6.67; I, 57.18.

The substance is therefore diiodomaleylphenylhydrazide. The same substance was obtained from phenylhydrazine and diiodomaleic anhydride in absolute alcohol or glacial acetic acid.

Calc.: I, 57.70; found: I, 57.19.

None of the red product was formed in this case.

Properties of Diiodomaleylphenylhydrazide.—It crystallizes in orange plates, which melt at 170° (uncor.) with decomposition and bubbling. It is soluble in alcohol, methyl alcohol, ether, chloroform, glacial acetic acid, benzene, toluene, nitrobenzene, or aniline; practically insoluble in carbon tetrachloride or naphtha. Dilute acids have no apparent action even if hot; strong sulfuric acid dissolves it with a brownish red color; dilute alkali does not act on it in the cold but dissolves it on heating.

The red product also obtained by the action of phenylhydrazine on diiodomaleic acid, occurred in such small quantities that it could not be studied thoroughly. The phenylhydrazomaleylphenylhydrazide would be expected, but our analyses do not accord well with this formula, and we could not get enough of it to repeat them. It crystallizes in red needles, melting with decomposition at 226° (uncor.). It is practically insoluble in the common organic solvents when cold; soluble in hot glacial acetic acid, benzene, or toluene.

Action of Water on Diiodomaleic Acid.—Two grams of diiodomaleic acid were heated to 100° in a sealed tube with 30 cc. of water for 3 hrs. Carbon dioxide was given off when the tube was opened; the other products were an aqueous solution and a brown oil. The solution contained hydriodic acid and formaldehyde in large quantity, and a little free iodine. The oil, which contained a few white crystals, solidified on standing, and, after it had been pressed in filter paper, was separated by heating it with naphtha into a soluble and an insoluble substance. As the work on these compounds was taken up at the end of the year, we have not been able to carry it beyond the preliminary stage. The soluble compound was purified by crystallization from naphtha until it showed the m. p. 95–96° (uncor.), when it was dried *in vacuo.*

Subst. 0.1362, 0.1807; AgI, 0.2036, 0.2694; Calc. for CHI_2COOH: I, 81.40; found: I, 80.80, 80.59.

These analyses indicate that this product is diiodoacetic acid, but our substance is white and melts at 95–96°, whereas the diiodoacetic acid, according to Angeli,[1] is yellow and melts at 110°. The explanation of these discrepancies must be left to future work. Our product is soluble in water, giving an acid reaction, and decomposing carbonates. It is also soluble in alcohol, ether, or benzene; practically insoluble in cold naphtha, soluble in hot, from which it is deposited in rosets of white needles. On exposure to the air it turns pink, and gives a test for free iodine. With lead acetate it gives a white precipitate, which can be crystallized from hot water.

The compound insoluble in naphtha, when crystallized from glacial acetic acid, gave white plates contaminated with a small quantity of white prisms, but the latter were removed by warming gently with water, after which the plates were crystallized several times from glacial acetic acid.

Subst. 0.2492; AgI, 0.4449; Calc. for C_2HI_5: I, 96.23; found: I, 96.49.

The substance therefore seems to be pentaiodoethane, but it is unfortunate that we did not have time to prepare enough for another analysis. It forms white plates melting at 182–184° (uncor.) and is soluble in alcohol, glacial acetic acid, or benzene, and insoluble in naphtha.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE OTHO S. A. SPRAGUE MEMORIAL INSTITUTE, LABORATORY OF CLINICAL RESEARCH, RUSH MEDICAL COLLEGE.]

THE SYNTHETIC PREPARATION OF *dl*-GLYCERIC ALDEHYDE.

BY EDGAR J. WITZEMANN.

Received July 14, 1914.

The synthetic preparation of *dl*-glyceric aldehyde was accomplished by Wohl at least fifteen years ago.[2] Several workers have repeated the synthesis on a small scale since that time. In those instances in which crystalline glyceric aldehyde was obtained it was by the use of seed crystals obtained from Wohl. Others have been satisfied to work with the uncrystallized syrup. For some chemical work, such as that of Schmitz[3] on the mechanism of acrose formation, such syrups would be fairly satisfactory, but for certain biochemical as well as chemical work the pure crystalline compound is necessary, in order that the experimental results shall be sharply significant. As a part of the program of work on the metabolism of sugars, which is being followed in this laboratory, it became necessary to prepare a quantity of pure crystalline glyceric aldehyde for biochemical experiments. In the course of this work certain improvements were made in the method of preparation, especially in the manip-

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[1] *Ber.*, **26,** 596 (1893).

[2] Wohl, *Ber.*, **31,** 1797, 2394 (1898); Wohl and Neuberg, *Ber.*, **33,** 3095 (1900).

[3] *Ber.*, **46,** 2327 (1913).