found to be readily obtained in a very pure state in almost the calculated quantity when the two components were coupled in an acetic acid medium, and after only one recrystallization from alcohol gave orange-yellow needles of m. p. 187°. Its yellow alcoholic solution, on the addition of ferric chloride, assumes a deep brown color and the solution in concd. sulfuric acid is red.

Anal. Subs., 4.372: CO_2, 11.558; H_2O, 1.875. Subs., 3.988: N_2, 0.578 cc. (21°, 760.4 mm.). Calcd. for $C_{15}H_{11}ON_3$: C, 72.29; H, 4.42; N, 16.87. Found: C, 72.10; H, 4.77; N, 16.66.

The hydrochloride gave orange needles; m. p. 227° (decomp.). On pouring into water, it readily undergoes hydrolysis with the separation of the free base.

Anal. (Water of crystallization). Subs., 0.5407: H_2O, 0.0513. Calcd. for $C_{15}H_{12}ON_2Cl \cdot 1^1/_2H_2O$: H_2O, 9.05. Found: H_2O, 9.49. Subs., 0.2550: AgCl, 0.1321. Calcd. for $C_{15}H_{11}ON_2 \cdot HCl$: HCl, 13.44. Found: HCl, 13.17.

Furthermore, the disazo compound could also be obtained by the alcoholic alkaline coupling of the mono-azo compound with diazobenzenechloride, but its quality was found to be far inferior after repeated recrystallizations from alcohol.

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The Direct Nitration of Furfural.—In continuation of studies concerned with substitution reactions of sensitive furan types,[1] it was found possible to prepare 5-chloro-2-furfural by chlorination not only of furfural diacetate but also of furfural. This suggested that it might be possible to nitrate furfural directly, and so avoid the prior, independent preparation of furfural diacetate. Experiments have confirmed this expectation.

Using the same molar proportions and technique described previously, the yield of nitrofurfural *diacetate* obtained from 96 g. (1 mole) of freshly distilled furfural was 110 g., or 45%, melting at 85°. When crystallized from hot alcohol, the yield of pure nitrofurfural diacetate melting at 92° was 80 g., or 33%.

In the treatment with alkali subsequent to nitration of the furfural, sufficient sodium hydroxide is added to the iced mixture to give a faint but distinct alkaline reaction to litmus. The oil obtained in this manner is separated by decantation from the aqueous solution, and then warmed with sufficient pyridine (not less than 250 cc.) to effect complete solution. The

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[1] Gilman and Wright, THIS JOURNAL, **52**, 2550 (1930); see also, Gilman and Wright, *ibid.*, **52**, 1170 (1930).

acetic acid removed in this manner from the intermediate compound, which may or may not be a product of ring scission, can also be removed by means of other bases like dimethylaniline. The nitrofurfural is readily obtained, if necessary, by hydrolysis[1] of the crude diacetate.

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A Note on the Preparation of Glycine.—The classical method of preparing glycine through the interaction of chloro-acetic acid and ammonia with the subsequent formation of the copper or lead salt has been abandoned by Clarke and Taylor[1] in favor of a method involving the hydrolysis of methylene-amino-acetonitrile. The starting material is fairly expensive and the yield of 31–37% is not high. Robertson,[2] after a study of the velocity and course of the reaction between chloro-acetic acid and ammonia, recommends the use of a large excess of ammonia. When the molecular ratio of ammonia to chloro-acetic acid is 60:1, the actual concentration of glycine in solution is increased to 86%. He eliminates the ammonium chloride by means of silver oxide and obtains a final yield of 50% of pure glycine.

It was thought that a correspondingly large yield of pure glycine could be obtained by making use of this high ratio of ammonia to chloro-acetic acid, and crystallizing the glycine directly from the concentrated reaction mixture in the presence of pyridine according to the method of Clarke and Taylor or in the presence of aniline as suggested by Benedict,[3] thus eliminating the time and expense involved in the use of silver oxide to remove the ammonium chloride. The attempt proved successful and the following method was worked out.

Two moles of chloro-acetic acid (189 g.) is dissolved in 8 liters of ammonium hydroxide (sp. gr. 0.90) in a 12-liter flask and allowed to stand at room temperature for forty-eight hours. The excess of ammonia is distilled off and recovered. The mixture is concentrated, *in vacuo* if preferred, until precipitation of ammonium chloride begins. The salt is dissolved by warming on the steam-bath with the addition of the smallest possible volume of water. If the solution is not clear, it is filtered by suction. The filtrate and washings should occupy a volume of about 500 cc. A

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[1] Clarke and Taylor, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. IV, p. 31.

[2] Robertson, THIS JOURNAL, 49, 2889 (1927).

[3] Benedict, *ibid.*, 51, 2277 (1929).