NOTES

The β-Chlorovinyl-arsines.[1]—The work of Miller and Witherspoon[2] has shown that the compound obtained by reacting β-chlorovinyl-dichloro-arsine with diphenylamine is not 6-β-chlorovinyl-phenarsazine, as reported in the above entitled article, but 6-chloro-phenarsazine. The compound is extremely difficult to obtain pure by crystallizing from solvents. Five crystallizations from xylene gave a product melting at 189° (uncorr.). By vacuum sublimation, Miller reports a melting point of 193–194°.

Similar correction should hold for the product obtained when phenyl-α-naphthylamine is condensed with β-chlorovinyl-dichloro-arsine. Thus in both cases the amines apparently condense with arsenic chloride, present as a result of decomposition or equilibrium, giving a chloro-arsine and not a chlorovinyl-arsine.

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Preparation of Benzene-azo Derivatives of 8-Hydroxyquinoline.—According to J. Mathëus,[1] the alkaline coupling of 8-hydroxyquinoline with diazobenzene-chloride gives 5-benzene-azo-8-hydroxyquinoline. In the present work, which was executed to obtain such a compound for use in the Skraup reaction with certain azo compounds, when diazobenzene-chloride and 8-hydroxyquinoline were coupled in equimolecular proportion in an alkaline medium with as small an amount of water as possible, the chief product obtained was found to be 5,7-benzene-disazo-8-hydroxy-quinoline, which after three recrystallizations from alcohol gave deep violet crystals of excellent purity; m. p. 205–206°; yield, 16 g. from 14.5 g. of 8-hydroxyquinoline. Its alcoholic solution assumes a red color, and the solution in concd. sulfuric acid is indigo blue, but on addition of alcohol the color changes to violet red.

Anal. Subs., 6.320: CO_2, 16.558; H_2O, 2.488. Subs., 3.115, 1.897: N_2, 0.576 cc. (30°, 762 mm.) 0.344 cc. (31°, 756 mm.). Calcd. for $C_{21}H_{15}ON_5$: C, 71.39; H, 4.25; N, 19.83. Found: C, 71.45; H, 4.37; N, 20.08, 19.41.

On the other hand, when the coupling was conducted in a very dilute solution, the mono-azo compound was the chief product, which after four recrystallizations from alcohol gave brownish-yellow needles (m. p. 185–186°); its properties were identical with those of 5-benzene-azo-8-hydroxy-quinoline given by Mathëus. The mono-azo compound, however, was

[1] "The β-Chlorovinyl-arsines and their Derivatives," W. Lee Lewis and H. W. Stiegler, This Journal, **47**, 2546 (1925).

[2] Unpublished, Chemical Division, Edgewood Arsenal, Maryland.

[1] Mathëus, *Ber.*, **21**, 1644 (1888).

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 diazobenzene-chloride, 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

[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

[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).

mixture of 800 cc. of methyl alcohol and 140 cc. of pyridine is stirred in. Crystallization of the glycine begins at once. After standing overnight, the glycine is filtered off, suspended in methyl alcohol, filtered and washed with methyl alcohol. A yield of 96 g. or 64% is obtained. A further yield of 2 to 3 g. may be secured from the combined mother liquor and washings on standing. If an attempt is made to crystallize the glycine from a warm solution of much greater concentration than the one suggested, the product will be contaminated with considerable ammonium chloride. This may be almost completely removed by washing with methyl alcohol. The glycine is recrystallized by dissolving in 300 cc. of water with warming. In order to remove the last traces of ammonia, 6 g. of permutit is added and after thorough stirring the mixture is filtered through a charcoal mat. The solution with washings should occupy about 400 cc. and should be crystal clear; 800 cc. of methyl alcohol is stirred in and the mixture is allowed to stand overnight until crystallization is complete. The glycine is filtered off and washed with methyl alcohol. The yield is 81 g. or 54%. The product is free from the chloride ion and from ammonia, as shown by testing with Nessler solution. It melts at from 225–230° (corr.), and shows the theoretical percentage of nitrogen and amino nitrogen. An equivalent amount of aniline may be substituted for the pyridine if desired in the first crystallization but the product carries a slight yellow color. This is completely removed on recrystallization.

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o-Phenetylurea.—On account of its industrial importance, dulcin has received considerable attention while the corresponding ortho derivative has been slighted. The writer finds but one literature reference in a paper by Pierron,[1] who prepared this compound from *o*-ethoxyphenylcyanamine as a means of identification of the latter. He quotes a melting point of 206°, which appears to be too high. It seemed worth while to make the compound principally in order to compare its properties with those of dulcin derivatives now in preparation.

A 5-g. portion of *o*-phenetidine is treated with 40 cc. of water and 2.5 cc. of concentrated hydrochloric acid. A solution of 2.25 g. of potassium cyanate in 20 cc. of water is added in small portions with a thorough shaking between additions. Precipitation is complete in about ten minutes. After filtration the solid is washed with dilute ammonium hydroxide and then with ether. It is at once recrystallized from hot dilute ethanol to

[1] Pierron, *Ann. chim. phys.*, [7] **15**, 145 (1908).

which sufficient ammonium hydroxide is added to give a decided odor. The crystals are washed with ether. When dry the purification is completed by a recrystallization from hot benzene; yield, 2 g.; white microscopic needles. The compound shows a slight shrinkage at about 139° and melts at 142–143°. It is tasteless and odorless. Concentrated sulfuric acid gives a colorless solution which upon heating becomes a faint straw color.

Anal. Calcd. for $C_9H_{12}O_2N_2$: C, 60.0; H, 6.66; N, 15.56. Found: C, 60.10; H, 6.72; N, 15.64.

The compound is soluble in hot water, ethanol, amyl alcohol and hot benzene. It is very slightly soluble in ether.

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COMMUNICATIONS TO THE EDITOR

DR. C. S. HUDSON'S VIEWS ON THE RELATIONSHIP OF STRUCTURE TO THE OPTICAL ROTATIONS OF SUGARS

Sir:

Dr. C. S. Hudson has not utilized the means which were open to him to test the validity of his views by direct chemical experiments. The basis on which he develops his argument is the presumed existence, which his statistical methods enable him to detect, of a new form of mannose (calculated $[\alpha]_D$ +77°) in derivatives of 4-glucosido-mannose, obtainable from cellobiose through cellobial. If this foundation for his scheme fails, then the entire superstructure of rival formulas which he has raised upon it must collapse.

A survey of his two recent papers [THIS JOURNAL, **52**, 1680, 1707 (1930)] has led me to select for this critical test an experimental method which he has tacitly approved: he has accepted and utilized the observation of Fischer and Armstrong that β-methylmaltoside gives rise by enzyme hydrolysis to β-methylglucoside without ring change. Implicit in Dr. Hudson's scheme, therefore, is the expectation that 4-glucosido-α-methylmannoside will yield by enzyme cleavage his hypothetical α-methylmannoside ($[\alpha]_D$ +125°), inasmuch as this is the glycoside of the unknown form of mannose to which he has assigned the 1,5-ring.

With my colleague Dr. E. L. Hirst and other co-workers (R. J. W. Reynolds, H. R. L. Streight, H. A. Thomas, J. I. Webb and Miss M. Plant) I have prepared and investigated the chemical behavior of both 4-glucosido-α-methylmannoside and 4-galactosido-α-methylmannoside to which the 1,4-ring cannot apply since the 4-position in the mannose residue is occupied by the biose link. Both these substances are hydrolyzed by