

NOTES

The β -Chlorovinyl-arsines.¹—The work of Miller and Witherspoon² 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-hydroxyquinoline, 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: CO₂, 16.558; H₂O, 2.488. Subs., 3.115, 1.897: N₂, 0.576 cc. (30°, 762 mm.) 0.344 cc. (31°, 756 mm.). Calcd. for C₂₁H₁₅ON₅: 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-hydroxyquinoline 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² Unpublished, Chemical Division, Edgewood Arsenal, Maryland.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: CO₂, 11.558; H₂O, 1.875. Subs., 3.988: N₂, 0.578 cc. (21°, 760.4 mm.). Calcd. for C₁₅H₁₁ON₃: 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: H₂O, 0.0513. Calcd. for C₁₅H₁₂ON₂Cl·1½H₂O: H₂O, 9.05. Found: H₂O, 9.49. Subs., 0.2550: AgCl, 0.1321. Calcd. for C₁₅H₁₁ON₂·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

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