The Preparation of Acetylchloro-aminobenzene.—The physical and chemical properties and the rate and mechanism of the rearrangement of acetylchloro-aminobenzene have been investigated recently in several laboratories.[1] Since the presence of impurities such as acetanilide affect the rearrangement in aqueous solution[1c,2] and in glacial acetic acid,[1c,2] it is desirable to have a method of preparation which will produce acetylchloro-aminobenzene without contamination with other anilides. A method is outlined below which can be relied upon to give a 70% yield of pure acetylchloro-aminobenzene melting at 91° and requiring no further purification.

(A) To a solution of 15 g. of acetanilide (0.11 mole) in 3 liters of water, 16.8 g. of sodium bicarbonate (0.2 mole) is added and the whole is filtered to remove suspended particles.

(B) To 150 cc. of 1.0 *M* sodium carbonate chlorine gas is added until the solution contains between 1.6×10^{-3} and 1.8×10^{-3} equivalents of chlorine per cc. as determined by analysis of a portion. This is prepared at 5° and the solution is filtered before using.

Solution A is kept at approximately 5° and is stirred slowly by a mechanical device during the dropwise addition of a calculated volume of Solution B. (Too rapid stirring of A may cause precipitation of acetanilide.) The product, acetylchloro-aminobenzene, precipitates toward the end of the addition of the chlorine solution. After standing for about fifteen minutes to insure complete precipitation, the needle-like crystals are removed by filtration, washed with cold water until no further test for chloride ion is obtained and dried at room temperature in a vacuum desiccator over sulfuric acid; yield, 13 g., melting point 90.5–91°.[3]

The product may be recrystallized from a solvent composed of 1 part of acetone and 9 parts of petroleum ether, yielding plate-like crystals which have the same melting point as the needles.

Armstrong[4] prepared the substance at elevated temperatures. (50–85°) and obtained fine needles. Chattaway and Orton[5] replied to his statement as to the crystal form as follows: "Acetylchloro-aminobenzene, from whatever solvent it separates, crystallizes, according to our observations in plates or short, four-sided prisms. When needles are present, they are undoubtedly the isomeric *p*-chloro-acetanilide. . . . ." The discovery that the compound may be prepared in either form settles a dispute of long standing.

The method here presented differs from others in use up to the present time in that a sodium bicarbonate buffer is present in the acetanilide solution, which prevents the formation of *o*- and *p*-chloro-acetanilide even

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[1] (a) Mathews and Williamson, This Journal, **45**, 2574 (1923); (b) Orton, Soper and Williams, *J. Chem. Soc.*, 998 (1928); (c) Soper, *J. Phys. Chem.*, **31**, 1193 (1927); (d) Bradfield, *J. Chem. Soc.*, 351 (1928); (e) Porter and Wilbur, This Journal, **49**, 2145 (1927).

[2] Porter and Barnes, paper ready for publication.

[3] Since the compound decomposes on heating, samples should be placed in the bath, which is already at 82–83°. Then with the usual rate of heating, the product, if pure, will melt at 90.5–91°.

[4] Armstrong, *J. Chem. Soc.*, **77**, 1047 (1900).

[5] Chattaway and Orton, *ibid.*, **79**, 274 (1901).

though a chlorine solution is used which is three times the maximum concentration considered safe by Chattaway and Orton.[6] The method is rapid and the product is better than 99.7% pure.

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Note on Caryophyllin and Urson.—In a previous article[1] the writer reported the results of an examination of caryophyllin and urson, two very similar and probably isomeric compounds, having apparently the composition $C_{30}H_{48}O_3$ and exhibiting properties which could best be explained by the assumption of an oxy-lactone structure, or the grouping $\left\{\begin{matrix}-\mathrm{OH}\\ -\mathrm{O}-\rceil\\ -\mathrm{CO}\rfloor\end{matrix}\right.$

More recently urson has been studied by van der Haar,[2] who has arrived at the conclusion that the alternative formula, $\left\{\begin{matrix}-\mathrm{OH}\\ -\mathrm{COOH}\end{matrix}\right.$, which is that of an hydroxy acid, has been demonstrated. The arguments against this formula have already been noted by the writer. Van der Haar also criticizes the methods employed by the writer as "uncontrolirbar" in comparison with elementary analyses, but in reality, the titrations used to show the functional relations of these compounds can be "controlled" or checked with the utmost ease, and they were employed exactly because they are more conclusive and satisfactory for the purpose in view than combustions.

It was found that caryophyllin and urson could be titrated with accuracy in alcoholic solution, the results indicating one carboxyl or lactone group in the C_{30} molecule. On acetylation, two acetates were obtained; one, an unstable diacetate, convertible by boiling with alcohol into a stable mono-acetate, which in turn yielded the original caryophyllin or urson by hydrolysis with alkali. These results appeared to be explainable only by the oxy-lactone formula. Van der Haar, however, obtained from urson an acetate, melting at 200°, which on boiling with alcohol gave a compound melting at 275°, which without further examination he assumed to be urson. Inasmuch as urson melts at about 285° and the mono-acetate at about 265°, the identification is rather unsatisfactory. In view of the importance of this fact for his hypothesis, a more thorough examination of the product would have been desirable. A quantitative hydrolysis would have been conclusive. In two later articles[3] van der Haar has revised his previous

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[6] Chattaway and Orton, *J. Chem. Soc.*, **75**, 1046 (1899).

[1] Dodge, THIS JOURNAL, **40**, 1917 (1918).

[2] Van der Haar, *Rec. trav. chim.*, **43**, 367, 542 (1924).

[3] Van der Haar, *ibid.*, **46**, 775 (1927); **47**, 585 (1928).