The residue was warmed with 20% aqueous potassium hydroxide, cooled, filtered off, washed and dried. Extracting the mother liquor with ether gave more of the product. The quinoline-4-methanol was purified by distilling *in vacuo*, b. p. 145° at 0.2 mm., and crystallizing from benzene; yield 50–60%, m. p. 96–97° (uncor.).

Anal. Calcd. for $C_{10}H_9NO$: C, 75.43; H, 5.70; N, 8.81. Found: C, 75.43, 75.68; H, 5.89, 5.88; N, 9.05, 8.89.

Heating under certain conditions converted the product into a higher melting substance.

Phenylurethan of 4-Quinolinemethanol.—From the components at 100°, crystallized from alcohol, m. p. 159.5–160.5° (uncor.).

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: N, 10.06. Found: N, 9.86, 10.02.

BANTING AND BEST DEPARTMENT OF MEDICAL RESEARCH
UNIVERSITY OF TORONTO
TORONTO, CANADA

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Preparation of Benzaldehyde from Benzene

BY WILLIAM J. KING AND PATRICK T. IZZO

In previous reports from this Laboratory,[1,2] the use of sodium cyanide instead of hydrogen cyanide in the Gattermann synthesis of aldehydes has been shown to be applicable to aromatic hydrocarbons.

In an extension of this investigation it has now been found that contrary to the statements in the literature[3] sodium cyanide can be used satisfactorily to replace hydrogen cyanide even for the preparation of benzaldehyde from benzene. A maximum yield of 14% benzaldehyde has been obtained. Additional quantities of aluminum chloride did not increase the yield of aldehyde beyond this percentage. Augmenting the proportionate amount of sodium cyanide caused the yield of benzaldehyde to drop.

Procedure.—Into a mixture of 400 g. (3 moles) of anhydrous aluminum chloride and 50 g. (1 mole) of sodium cyanide in 200 cc. (2.25 moles) of benzene in a 3-necked flask with a mercury-sealed stirrer and an efficient reflux condenser, dry hydrogen chloride was passed for twenty minutes. The mixture was then boiled on a water-bath and the boiling, stirring and introduction of the hydrogen chloride continued for eleven hours.

At the end of this period, the reaction mixture was cooled and poured on a large amount of ice and hydrochloric acid contained in a three-liter, round-bottom flask. The mixture was refluxed under the hood for about an hour to expel excess hydrogen cyanide and to complete the hydrolysis of the phenylmethyleneformamidine hydrochloride.[4] It was then steam-distilled for two to three hours and the distillate extracted with ether, the extract being dried with anhydrous sodium sulfate. The ether was then distilled off and the residue fractionated. The first fraction, mostly benzene, was collected at 75–100°, the second at 100–160°, the third at 160–185°.

The third fraction was rectified and 20 g. of a liquid boiling at 176–180° was obtained. This compound was characterized by its semicarbazone, m. p. 222° (cor.).

Anal. (benzaldehyde). Calcd.: C, 79.24; H, 5.66. Found: C, 79.07; H, 5.86.

The first fraction (75–100°) was about 30 cc. Assuming this to be mostly benzene, then subtracting this amount from 200 cc., we found that 170 cc. (149 g.) of benzene underwent reaction from which 20 g. of the aldehyde was obtained. On this basis the yield was about 14%.

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[1] Niedzielski and Nord, THIS JOURNAL, **63**, 1462 (1941).

[2] Niedzielski and Nord, *J. Org. Chem.*, **8**, 147 (1943).

[3] J. E. Jones, "Synthetic Organic Chemicals," (Eastman Kodak Company) 15, No. 2 (1943).

[4] Hinkel, Ayling and Morgan, *J. Chem. Soc.*, 339 (1936).

The Purification of Acetone by the Shipsey–Werner Method

BY ROBERT LIVINGSTON

The Shipsey–Werner[1] method of purifying acetone, which involves the formation of the solvate, $NaI\cdot 3C_3H_6O$, is commonly used for small scale laboratory purifications. This method (which was quoted in 1935 by Weissberger and Proskauer[2]) was published before the detailed data on the solubility of NaI and $NaI\cdot 3C_3H_6O$ in acetone[3,4,5] were available. In light of the latter information, the procedure can be improved in respect both to yield and to convenience. The following outline has been tested and proved to be satisfactory.

Saturate acetone with dry sodium iodide at about 25° (between 25 and 30°). Decant the solution from the excess solid. Cool the solution to as low a temperature as can be conveniently maintained during filtration, etc. With ordinary equipment a temperature of about $-10°$ is satisfactory. Filter off the mother liquor on a Buchner or sintered glass filter. Transfer the cold salt to a flask and warm to about 30° ($>26°$). Decant the liquid into a distilling flask, distill, rejecting the last 10%.

Saturating the acetone with sodium iodide at approximately room temperature (25 to 30°), rather than at the boiling point of the solvent (2), has two advantages. First, it is more convenient; and, second, it results in an increase in the theoretical yield of purified acetone from about 23 to about 35%. The step of warming the solvated salt above its transition point and decanting the liquid into the distilling flask, is introduced largely to avoid the awkward transfer of a moist solid; but it has the additional advantage that the salt cake, remaining in the flask after distillation, is reduced by about 40%.

Precautions: Contamination of the salt, solvent or vessels by acids or by salt of heavy metals (such as iron or copper) should be avoided. Manipulation of the chilled solvent should be planned to

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[1] K. Shipsey and E. A. Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

[2] A. Weissberger and E. Proskauer, "Organic Solvents," Oxford Press, 1935, p. 142.

[3] R. Macy and E. W. Thomas, THIS JOURNAL, **48**, 1547 (1926).

[4] A. E. Wadsworth and H. M. Dawson, *J. Chem. Soc.*, **129**, 2784 (1926).

[5] W. R. G. Gell, C. B. Rowlands, I. J. Bamford and W. J. Jones, *ibid.*, 1930 (1927).

minimize the time it is in contact with the (moist) laboratory air.

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An Improved Procedure for the Replacement of Aromatic Amino Groups by Bromine

By Melvin S. Newman and William S. Fones[1]

The replacement of aromatic amino groups by bromine by the Sandmeyer or Gattermann method is frequently unsatisfactory with regard to the time and apparatus required, the low yield, or both. The Schwechten[2] procedure is often considerably better but suffers from the high cost of reagents. Therefore an improved procedure is highly desirable.

TABLE I

Amine	Product	Yield[a] pure (crude), %
o-Chloroaniline	*o*-Bromochlorobenzene	85 [89–95][a]
m-Chloroaniline	*m*-Bromochlorobenzene	46[b] [91–94]
p-Chloroaniline	*p*-Bromochlorobenzene 4-Chloro-2,6-dibromophenol	77 (81)[b] [83] 8[b]
o-Nitroaniline	*o*-Bromonitrobenzene	83 (93) [80]
m-Nitroaniline	*m*-Bromonitrobenzene	87 (92) [75]
p-Nitroaniline	*p*-Bromonitrobenzene	79 (97) [90]
p-Nitroaniline	*p*-Chloronitrobenzene	33[c]
m-Toluidine	*m*-Bromotoluene	3[b]
Ethyl anthranilate	*o*-Bromobenzoic acid and 3,5-Dibromosalicylic acid	20 (32) 23
Anthranilic acid	*o*-Bromobenzoic acid and 3,5-Dibromosalicylic acid	
3-Nitro-5-aminobenzoic acid	3-Nitro-5-bromobenzoic acid	79
Ethyl 2,4-dichloro-5-aminophenoxyacetate	2,4-Dichloro-5-bromophenoxyacetic acid	59[e]
Sulfanilic acid	2,4,6-Tribromophenol	40
p-Anisidine	*p*-Bromoanisole	7
1-Naphthylamine	1-Bromonaphthalene	20
2-Naphthylamine	Only tars	. .
α-Aminopyridine	*α*-Bromopyridine	35
n-Butylamine	Mixture	. .[d]

[a] The yields indicated are for pure product having properties in agreement with the literature values. Those yields were obtained by following the general procedure herein described. Since this was worked out for *o*-chloroaniline, the yields in the other cases are probably not the optimum. The figures in parentheses indicate crude yields and the yields in brackets are the best reported for the Sandmeyer procedure for the corresponding compounds in the following articles: Fry and Grote, THIS JOURNAL, **48**, 710 (1926); Hartwell, "Organic Syntheses," John Wiley & Sons, New York, N. Y., 1944, Vol. 24, pp. 22–24. [b] Anhydrous hydrogen bromide to saturation was used in place of 40% acid. [c] Concentrated hydrochloric acid was used instead of hydrobromic acid. [d] A mixture which contains some butyl bromide was obtained but was not further investigated. [e] New compound, m. p. 159–161°. *Anal.* (Arlington Laboratories). Calcd. for $C_8H_5O_3Cl_2Br$: C, 32.0; H, 1.7. Found: C, 32.4, 32.3; H, 2.3, 2.1.

In 1875, Hubner[3] converted 3-amino-5-nitrobenzoic acid into 3-bromo-5-nitrobenzoic acid in unstated yield by passing nitrogen trioxide into a cooled solution of the amine in acetic and hydrobromic acids followed by heating of the resulting mixture until the evolution of nitrogen ceased. On repetition of this experiment, we obtained an 80% yield. In view of the simplicity of this procedure and the high yield of product we have studied this method in some detail. The results we have obtained with nineteen amines are summarized in Table I.

General Procedure

A stirred solution or suspension of the amine hydrobromide prepared from 0.1 mole of amine, 125 cc. of acetic acid and 50 cc. of 40% hydrobromic acid is maintained at 5–10° while nitrogen trioxide[4] is passed in until a permanent dark color appears. This usually requires about forty-five minutes, during which time any solid amine hydrobromide disappears. The solution is then slowly heated until a brisk evolution of nitrogen occurs. This is usually in the 40–50° range and free bromine is evident in the escaping gas. When the gas evolution slows, the reaction mixture is heated to reflux for a few minutes after which it is cooled somewhat and poured into an excess of 20% sodium hydroxide. The product is then isolated by suitable means. The heating phase of the reaction requires about thirty minutes.

The yields in the case of *o*-chloroaniline were less if any of the following conditions prevailed: 1, no stirring during addition of nitrogen trioxide (78%); 2, nearly pure nitrogen tetroxide replaced nitrogen trioxide (72%); 3, no excess hydrobromic acid (<20%); 4, only 2 equivalents of nitrogen trioxide passed in (68%); 5, slight excess of amine hydrobromide over nitrogen trioxide (9%). With *p*-chloroaniline, anhydrous hydrogen bromide in acetic acid improved the yield considerably (60 with 40% aqueous to 81% with anhydrous). No *m*- or *p*-bromotoluene was obtained when aqueous hydrobromic acid was used.

The results are consistent with the concept that a perbromide of the diazonium compound is formed and then decomposed by heat, as shown

$$\mathrm{RNH_2.HBr} \xrightarrow{N_2O_3} \mathrm{RN_2Br} + \mathrm{Br_2} \longrightarrow \mathrm{RN_2Br_3} \longrightarrow \mathrm{RBR} + \mathrm{N_2} + \mathrm{Br_2}$$

This explanation is supported by the following facts: (A) It is necessary to have hydrobromic acid in excess of that needed to form the amine hydrobromide. (B) Free bromine is present in large amount after the heating period but not before. (C) If sodium bisulfite is added before the heating period no organic bromide is formed. (D) It is known that diazonium salts react with bromine to form diazonium perbromides.[5]

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[1] This material is taken from a thesis presented by William S. Fones to the Graduate School in partial fulfilment of the requirements for the Ph.D. degree, December, 1946.

[2] Schwechten, *Ber.*, **65**, 1605 (1932); Newman and Wise, THIS JOURNAL, **63**, 2847 (1941).

[3] Hubner, *Ann.*, **222**, 166 (1884). It is interesting that this publication appeared before Sandmeyer's article on the use of cuprous bromide, *Ber.*, **17**, 1633 (1884).

[4] In our first experiments the oxides of nitrogen were generated by treating arsenic trioxide with nitric acid. Later nitrogen trioxide was obtained in steel cylinders from the du Pont Company.

[5] Griess, *Ber.*, **18**, 965 (1885).