A New Method for Deamination of Naphthylamines[1]

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Received September 25, 1973

The Schwechten reaction[3] consists in the heating of a complex of an aromatic diazonium salt and mercuric bromide, 1, to yield an aryl bromide, 2 (eq 1). These water-insoluble salts are formed by treating solutions of aryldiazonium salts with mercuric bromide. The yields of salts 1 are generally very high but the yields of 2 are not over 70%.[4]

$$\underset{\mathbf{1}}{(ArN_2^+)_2HgBr_4^{2-}} \xrightarrow{\Delta} \underset{\mathbf{2}}{2ArBr} + 2N_2 + HgBr_2 \qquad (1)$$

We sought a solvent for the salts in the hope that the decomposition to aryl bromides might be facilitated by the use of powdered glass. Because of successes in the use of a finely divided solid (powdered glass is only one of many solids that have been used) in the MacFadyen-Stevens reaction[5] and Pesci reaction,[6] we routinely examine the effect of added solids in reactions in which a gas is produced. When a solution of the salt formed from 7-chloro-1-naphthylamine was dissolved in hexamethylphosphoric triamide (HMPA), the evolution of nitrogen commenced at room temperature and was complete in about 20 min. If powdered glass was admixed the decomposition time was about 10 min. Surprisingly, however, the product was not the desired 7-chloro-1-bromonaphthalene but the deaminated product, 2-chloronaphthalene. Accordingly, our study was extended to other solvents and to other salts 1.

Although the salts 1 were moderately soluble in pyridine, dimethyl sulfoxide (DMSO), and *N*-methylpyrrolidone (NMP) and gas was evolved (but not quantitatively), the products were not produced in as high a yield as in the case of HMPA and the yields of monomeric substances were poor. Accordingly, only the reactions in HMPA were studied further. The results obtained are listed in Table I and the experimental details are discussed in the Experimental Section. In all cases the main compound obtained was the product in which the diazonium grouping had been replaced by hydrogen. Only trace amounts of substituted naphthyl bromides were formed. The only source for the hydrogen which replaces the diazonium grouping is the *N*-methyl group, but no attempts were made to characterize the decomposition products of the solvent, HMPA.

Thus, a new method can be added to other methods which have been used for deamination.[7-11] The new method may be advantageous for the following two reasons: (1) after diazotization in aqueous acid the diazonium compound may easily be isolated as a water-insoluble complex by treatment with mercuric bromide (the complex may be collected rapidly and washed with acetone to yield a readily dried salt), and (2) the reaction with HMPA can be completed in 10-20 min at room temperature. The yields of products were about the same whether powdered glass was used or not. In all of the reported experiments powdered glass was used.

Since the decomposition of arenediazonium hexafluorophosphates in tetramethylurea at 20-65° has been reported to result in deamination,[9] we dissolved *p*-toluenediazonium hexafluorophosphate in HMPA. There was an immediate exothermic reaction with evolution of nitrogen to yield 62% of toluene. Since this yield is greater than that reported when tetramethylurea was used (25-30%)[9,12] we conclude that HMPA is probably preferable to other solvents for deamination of diazonium hexafluorophosphates.

Table I
Formation and Decomposition of Arenediazonium Mercuric Bromide Complexes

1-Amino-naphthalene substituent[a]	Registry no.	Mp[b] of $[ArN_2^+]_2$-$HgBr_4^{2-}$	Registry no.	Naphthalene yield,[c] %
None	134-32-7	104	50986-52-2	70
4-Bromo	2298-07-9	127	50986-53-3	77
5-Bromo	4766-33-0	140	50986-54-4	76
7-Chloro	50987-58-1	117	50986-56-6	93
7-Methyl	6939-34-0	101	50986-58-8	72
2-Aminonaphthalene	91-59-8	103	50986-59-9	94
Ethyl anthranilate	87-25-2	114	50986-60-2	71[d]

[a] The amines were diazotized and treated with mercuric bromide as described.[8] In all cases the yield of dried complex salt, 2, was 92-99%. [b] The melting point recorded is really a decomposition point and varies with the rate of heating. [c] The yields represent isolated compounds which were at least 95% pure by glpc. The small impurity was the corresponding compound in which bromine had replaced the amino group. [d] The product was diethyl diphenate.

Experimental Section

Preparation of Arenediazonium Bromide-Mercuric Bromide Complexes. These complexes were prepared essentially as described. The precipitated complexes were washed with water and acetone and were air dried. The yields and melting points (decomposition) are listed in Table I.

Decomposition of Arenediazonium Mercuric Bromide Complexes. In a typical experiment 0.01 mol of dried complex 1 was added through a wide rubber tubing to a flask containing 35 ml of HMPA and 2 g of powdered soft glass stirred magnetically at room temperature. The theoretical amount of nitrogen was usually evolved within 10 min and the temperature rose to 40-45°. The reaction mixture was filtered and the filtrate was diluted with water. The ether extract of the reaction products was washed with water, dilute acid, and dilute alkali. After drying by passage through anhydrous $MgSO_4$, the ether was distilled and the residue was vacuum distilled to yield naphthalene or the substituted (deaminated) naphthalene. All products were identified by comparison with authentic samples. In each a purity of greater than 95% was indicated by glpc of the entire distillate before purification. The glpc analyses were performed on an Aerograph Autoprep A-700 model gas chromatograph using a 10 ft × 0.25 in. column packed with 30% silicone gum rubber SE-30 on 45-60 mesh Chromosorb W.

References and Notes

(1) This work was supported by Public Health Service Research Grant No. CA 7394 from the National Cancer Institute.
(2) Postdoctoral Research Associate.
(3) Schwechten, *Ber.*, **65**, 1605 (1932).
(4) M. S. Newman and P. H. Wise, *J. Amer. Chem. Soc.*, **63**, 2847 (1941).
(5) M. S. Newman and E. G. Caflisch, *J. Amer. Chem. Soc.*, **80**, 862 (1958).
(6) M. S. Newman and M. C. Vander Zwan, *J. Org. Chem.*, **38**, 319 (1973).
(7) K. H. Saunders, "The Aromatic Diazo-compounds," Edward Arnold, London, 1949, pp 268-273.
(8) N. Kornblum, "Organic Reactions," Vol. II, Wiley, New York, N. Y., 1944, Chapter 7.
(9) See K. G. Rutherford and W. H. Redmond, *J. Org. Chem.*, **28**, 569 (1963), and references cited therein.
(10) J. Nakayama, M. Yoshida, and O. Simamura, *Tetrahedron*, **26**, 4609 (1970).
(11) J. I. G. Cadogan and G. A. Molina, *J. Chem. Soc., Perkin Trans. 1*, 541 (1973).
(12) In ref 9 the interaction of *o*-toluenediazonium hexafluorophosphate with tetramethylurea to form *o*-methylphenoxytetramethylamidinium hexafluorophosphate in 61% yield is reported.