Aniline and Other Aromatic Amines from Carboxylic Acids and Ammonia
A Metal-catalysed Process

By Gregory G. Arzoumanidis*† and Frank C. Rauch
(*American Cyanamid Company, Stamford, Connecticut* 06904)

Summary Copper or palladium salts of aromatic acids react with ammonia at 220 °C under pressure to form aromatic amines in good yields.

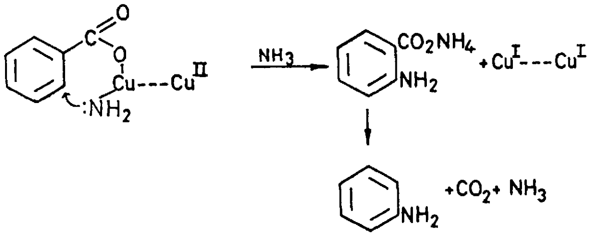
Copper or palladium benzoate in excess of benzoic acid reacts with NH_3 or aqueous NH_4OH in a closed system above 195 °C to yield $PhNH_2$, while Cu^{2+} is formally reduced to Cu^{+} [equation (1)]. By-products are diphenylamine and

$$2Cu(O_2CPh)_2 + 2NH_3 \xrightarrow{PhCO_2NH_4} 2CuO_2CPh + CO_2 + PhNH_2 + PhCO_2NH_4 \qquad (1)$$

phenol. Benzamide and benzonitrile are also formed from $PhCO_2NH_4$ in a non-oxidative side reaction. At 220 °C the aniline-forming reaction is complete in less than 30 min under an NH_3 pressure of less than 35 atm. Average yields based on Cu^{2+} as a limiting reagent are 72% aniline, 13% phenol, and 5% diphenylamine.

By-product phenol is produced by the thermal decomposition of copper benzoate[1] and no interconversion between aniline and phenol takes place under the conditions employed. Since ammoniacal solutions of Cu^{+} oxidize readily to Cu^{2+} in the air, a two-stage catalytic process has been developed, involving (i) the above reaction, and (ii) the reoxidation of Cu^{+}, with simultaneous separation of the products by steam distillation. Toluene is the industrial starting material in this process, since benzoic acid is produced by oxidation of toluene.

This novel decarboxylative amination of the aromatic ring proceeds most likely *via* a cyclic intermediate (Scheme). Indeed, the product isomer distribution from analogous reactions involving substituted benzoic acids indicate an exclusive *ortho*-attack, which strongly suggests the cyclic intermediate. Contrary to the direct synthesis of aniline by this method, phenol is produced *via* hydrolysis of *o*-benzoylbenzoic acid or phenyl benzoate.[1]



Scheme

The reaction may be performed successfully with a number of aromatic or heteroaromatic carboxylic acids which have the $-CO_2H$ group directly bonded to the ring.

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† *Present address:* Stauffer Chemical Company, Eastern Research Center, Dobbs Ferry, New York 10522.

[1] W. W. Kaeding, H. O. Kerlinger, and G. R. Cellins, *J. Org. Chem.*, **1965**, **30**, 3754, and references therein.