Selenocyanation of Aniline

T. H. Chao and R. E. Lyons, Indiana University

The new and successful method of thiocyanation by means of cupric thiocyanate as proposed by Kaufmann and Kuechler[1] encouraged us to investigate the possibilities of selenocyanation of the aromatic nucleus by reactions with cupric selenocyanate under similar conditions.

Experimental

Sodium selenocyanate was prepared by dissolving pulverized selenium in a warm concentrated aqueous solution of the theoretical quantity of sodium cyanide, contained in a distilling flask. The major portion of the water was then evaporated by passing a stream of laboratory fuel gas through the reaction mixture maintained at about 90°C., and finally, by additions of absolute alcohol followed by continued evaporations, the residue was obtained as a dry mass, which was preserved in absolute alcoholic solution of about 8% concentration.

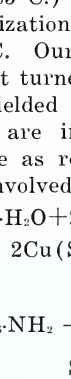
Cupric selenocyanate, prepared by reacting sodium selenocyanate with copper sulfate according to directions given by Fehling,[2] was unstable, decomposing rapidly into black cupric selenide and hydrogen selenide. No means was found for stabilizing or storing it without deterioration.

Para-selenocyano aniline—A yield of 40% was obtained by the following procedure: A mixture of 6 g. cupric acetate and 5 ml. acetic anhydride, to take up water of crystallization, was triturated constantly in a mortar during the gradual addition of 2.5 g. sodium selenocyanate in saturated absolute alcoholic solution and 0.5 g. aniline dissolved in 0.5 ml. glacial acetic acid. The reaction mixture after standing 0.5 hour was warmed to 60-65°C. for 2 hours, powdered and extracted with dry benzene. The p-selenocyano aniline obtained by evaporation, in partial vacuum, of the united benzene extracts was purified by resolution in warm benzene, adding dry gasoline until turbidity was established and warming until a clear solution resulted. Fine yellow needle like crystals (M.P. 85°C.) separated from the solution on standing and, after four recrystalizations from benzene-gasoline, melted with decomposition at 92-92.5°C. Our product was inactive with cold concentrated hydrochloric acid but turned red on boiling and, upon evaporation with acetic anhydride, yielded a white crystalline product (M.P. 206°C.). These deportments are in exact agreement with the properties of p-selenocyano aniline as reported by Challenger and co-workers.[3]

The reactions involved probably take place as follows:

(1) $Cu(CH_3{\cdot}COO)_2{\cdot}H_2O + 2NaSeCN \rightarrow Cu(SeCN)_2 + 2CH_3{\cdot}COONa + H_2O$

(2) $2Cu(SeCN)_2 \rightarrow 2Cu(SeCN) + (SeCN)_2$

(3) $(SeCN)_2 + C_6H_5{\cdot}NH_2 \rightarrow$  $+ HSeCN$

(4) $HSeCN \rightarrow HCN + Se.$

[1]H. P. Kaufmann and K. Kuechler, 1934. Ber. **67**:944.
[2]Herman V. Fehling, 1898. Neues Handwoerterbuch der Chemie. **6**:579.
[3]F. Challenger, A. T. Peters, J. Halvey, 1926. Jour. Chem. Soc. **1926**:1648. F. Challenger and A. T. Peters, 1928. Jour. Chem. Soc. **1928**:1375.

Attempts to extend this method of the synthesis of corresponding selenocyano compounds of toluene, chlorbenzene, monomethyl aniline, phenol, and anisol were unsuccessful. Moreover, the production of p-selenocyano aniline by this type of procedure was not satisfactory when mercuric acetate, ferric chloride, or stannic chloride was substituted for cupric acetate in the reaction mixture.