Chem. Pharm. Bull.
32(1) 348—349 (1984)

Formation of Cyanide Ion or Cyanogen Chloride through the Cleavage of Aromatic Rings by Nitrous Acid or Chlorine. VI. Evidence for Ring Cleavage of Benzene and Aniline

SABURO KANNO and TAKESHI OHYA*

Faculty of Pharmaceutical Sciences, Josai University, 1-1, Keyakidai, Sakado, Saitama 350-02, Japan

(Received May 19, 1983)

It was found that aniline [$^{13}C_6$] reacted with nitrous acid to give $^{13}CN^-$ and that benzene [$^{13}C_6$] or aniline [$^{13}C_6$] reacted with hypochlorous acid in the presence of ammonium ion to give $^{13}CNCl$. These results clearly indicate that the benzene ring was cleaved by nitrous acid or chloramine to give cyanide ion or cyanogen chloride.

Keywords——cyanide ion; cyanogen chloride; nitrous acid; chloramine; benzene [$^{13}C_6$]; aniline [$^{13}C_6$]; ammonium ion; hypochlorous acid

In the previous papers,[1-3] we reported that cyanide ion was formed by the reaction of aniline with nitrous acid and that cyanogen chloride was formed by the reaction of aromatic hydrocarbons, aromatic amines or phenolic compounds with hypochlorous acid in the presence of ammonium ion. These results suggest that the benzene ring was cleaved by nitrous acid or chloramine in the above reactions to give cyanide ion or cyanogen chloride. The purpose of this work was to confirm that the carbon atom of cyanide ion or cyanogen chloride formed by the above reactions originated from the benzene ring.

For this purpose, aniline [$^{13}C_6$] and benzene [$^{13}C_6$] were used as reaction materials. aniline [$^{13}C_6$] was reacted with nitrous acid, and the resulting $^{13}CN^-$, after conversion to $^{13}CNCl$ by chloramine-T treatment, was analyzed by mass fragmentography. Benzene [$^{13}C_6$] or aniline [$^{13}C_6$] was also reacted with hypochlorous acid in the presence of ammonium ion, and the resulting $^{13}CNCl$ was also analyzed by mass fragmentography.

In all cases, the resulting cyanogen chloride was $^{13}CNCl$. This result indicates that the carbon atom of cyanide ion or cyanogen chloride originated from the benzene ring (Chart 1).

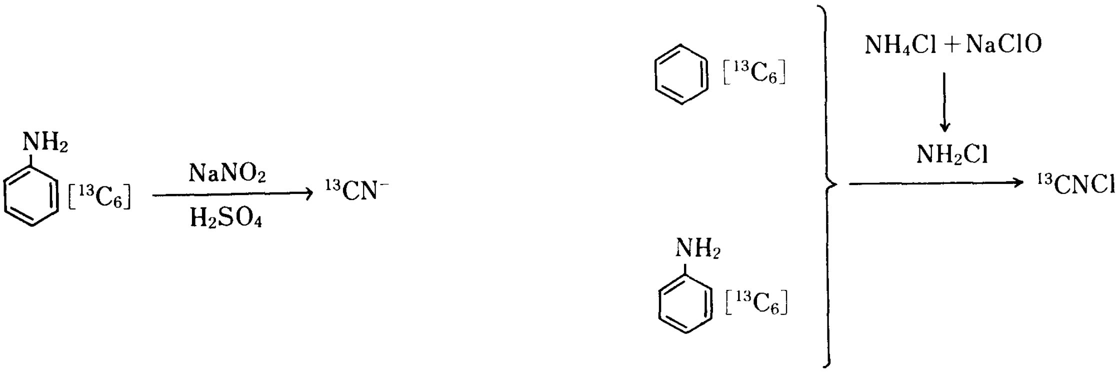

Chart 1

On the basis of these results, it has been confirmed that the benzene ring was cleaved by nitrous acid or chloramine in the above reactions to give cyanide ion or cyanogen chloride.

Experimental

Reagents——Benzene [$^{13}C_6$] (90.0 atom%), aniline [$^{13}C_6$] (90.0 atom%) and potassium cyanide [^{13}C] (90.0 atom%) were supplied by the British Oxygen Co., Ltd.

Cyanogen Chloride (^{12}CNCl and ^{13}CNCl) Standard Solutions——A round-bottomed flask containing 100 ml of 0.3 M phosphate buffer solution (pH 5.0), 5 ml of 1.0% chloramine-T aqueous solution and 1.0 ml of 1.0 μmol/ml potassium cyanide (KCN and K^{13}CN, respectively) aqueous solution was allowed to stand for 5 min, then nitrogen gas was bubbled through the solution and the gas released was passed through 20 ml of *n*-hexane cooled to $-30\,°C$. These solutions were used as cyanogen chloride (^{12}CNCl and ^{13}CNCl) standard solutions.

Gas Chromatography Mass Spectrometry (GC-MS)——A Shimadzu LKB 9000 machine was used. Separations were carried out on a glass column (2 m × 3 mm i.d.) packed with a 7% Halcomide on Chromosorb W. The column temperature was 55 °C, and the helium carrier gas flow was 10 ml/min. the ionization energy was 20 eV. The ions were measured at m/e 61 for ^{12}CNCl and m/e 62 for ^{13}CNCl.

Reaction Procedures——Reaction Procedure I: A mixture of 30 ml of distilled water, 1 mmol of aniline [$^{13}C_6$], 5 mmol of sodium nitrite and 5 ml of 1 N sulfuric acid aqueous solution in a round-bottomed flask was immediately distilled, and 20 ml of the distillate was taken into 10 ml of 1 N sodium hydroxide aqueous solution in a vessel, then used for the analysis of cyanide ion.

Reaction Procedure II: A mixture of 95 ml of 0.3 M phosphate buffer solution (pH 5.0), 1 μl of benzene [$^{13}C_6$] or 1 μl of aniline [$^{13}C_6$], 3 ml of 100 μmol/ml ammonium chloride aqueous solution and 5 ml of 100 μmol/ml sodium hypochlorite aqueous solution in a round-bottomed flask was allowed to stand for 1 h at room temperature, then used for the analysis of cyanogen chloride.

Analyses of Cyanide Ion and Cyanogen Chloride——Cyanide Ion: The whole solution obtained by reaction procedure I was acidified with 20 ml of 1 N sulfuric acid aqueous solution, and nitrogen gas was bubbled through the solution. The gas released was passed through 1 ml of 1 N sodium hydroxide aqueous solution, then 1 ml of *n*-hexane, 0.5 ml of 2 N sulfuric acid aqueous solution, 0.5 ml of 2 M sodium dihydrogen phosphate aqueous solution and 0.5 ml of 1.0% chloramine-T aqueous solution were added. The tube was capped, briefly shaken and allowed to stand in an ice bath. After approximately 5 min, the tube was shaken again and 1 μl of the *n*-hexane layer was injected into the GC-MS apparatus.

Cyanogen Chloride: Nitrogen gas was bubbled through the whole solution obtained by reaction procedure II. The gas released was passed through 20 ml of *n*-hexane cooled to $-30\,°C$. Ten microliters of the *n*-hexane solution was injected immediately into the GC-MS machine.

Acknowledgement The authors are grateful to Professor Shun-ichi Yamada of this university for his interest and encouragement throughout this work.

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