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Formation of Cyanide Ion or Cyanogen Chloride through the Cleavage of Aromatic Rings by Nitrous Acid or Chlorine. X.[1] Pathway of Cyanogen Chloride Formation in the Reactions of 1-Naphthol and 4-Phenylimidazole with Chloramine

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The pathway in the formation of cyanogen chloride from the reaction of 1-naphthol (**1**) and 4-phenylimidazole with chloramine was investigated. The intermediates isolated in the reaction of 1-naphthol (**1**) with chloramine were *N*-chloro-1,2-naphthoquinone 2-imine (**2**) and *o*-carboxycinnamonitrile (**6**), the latter of which, liberating cyanogen chloride, was finally converted to phthalide-3-carboxylic acid (**8**). The products obtained in the reaction of 4-phenylimidazole (**10**) with chloramine were benzonitrile (**14**), benzoylformic acid (**22**) and benzoic acid (**23**) besides cyanogen chloride. Cyanogen chloride formed by the reaction of 4-methylimidazole with [^{15}N]-chloramine was C^{14}NCl. From these results the pathway of cyanogen chloride formation was elucidated.

Keywords——cyanogen chloride; 1-naphthol; 4-phenylimidazole; histidine; chloramine; hypochlorous acid

Introduction

As is generally known, chloramine is widely generated as a by-product of the chlorination of public water and waste water, which commonly contain ammonium ion.[2-4] It is also generally accepted that phenolic compounds as a component of humic material and amino acids are often contained in natural water and waste water.[5-9]

In the previous papers,[10-13] we reported that cyanogen chloride was formed by the reactions of aromatic compounds such as aromatic hydrocarbons, aromatic amines, phenolic compounds and aromatic amino acids with hypochlorous acid in the presence of ammonium ion in a neutral aqueous solution at room temperature and that the formation of cyanogen chloride was due to the cleavage of the aromatic rings by chloramine. We also reported that cyanogen chloride was formed during chlorination of raw water sampled at water treatment plants and showed that the formation of cyanogen chloride might be due to the reaction of humic substances with chloramine.[14] This result suggests that chloramination reaction with organic compounds often occurs during the chlorination process. Although the chlorination reactions of organic compounds were studied in detail,[15-21] little is known of the chloramination reaction in aqueous solution. This study was intended to investigate the mechanism of cyanogen chloride formation by the reaction of aromatic compounds with chloramine.

In this paper, we describe the pathway of cyanogen chloride formation from 1-naphthol and 4-phenylimidazole. 1-Naphthol and 4-phenylimidazole were selected as model compounds for phenol and histidine, respectively, in order to facilitate the isolation and detection of the reaction products.

Experimental

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were measured with tetramethylsilane (TMS) or 3-

(trimethylsilyl)propionic acid-d_4 sodium salt (TSP-d_4) as an internal standard, with a JEOL GX270FT NMR spectrometer. Gas chromatography (GC) was performed on a Shimadzu 9A apparatus with a flame ionization detector using a glass column (3 mm i.d. × 2 m) packed with Tenax GC(60—80 mesh); injection temperature, 140 °C; column temperature, 80 °C; carrier gas, N_2 40 ml/min. GC-MS was performed on a JEOL DX-300 apparatus under the following conditions. (1) For the identification of $C^{14}NCl$ or $C^{15}NCl$: column, glass column (3 mm i.d. × 2 m) packed with Tenax GC (60—80 mesh); carrier gas, He 20 ml/min; column temperature, 85 °C; injection temperature, 140 °C; separator and ion source temperatures, 250°C; ionizing voltage, 70 eV. (2) For the identification of reaction products: column, glass column (3 mm i.d. × 2 m) packed with 5% Silicone SE-30 on Chromosorb WAW (60—80 mesh); carrier gas, He 20 ml/min; column temperatures, 90 °C (for benzonitrile) and 120 °C (for methyl benzoate and methyl benzoylformate); injection temperature, 200 °C; separator and ion source temperatures, 250 °C; ionizing voltage, 70 eV.

Materials——*N*-Chloro-1,2-naphthoquinone 2-imine (**2**), 2-chloro-1,4-naphthoquinone (**5**), *o*-carboxycinnamonitrile (**6**) and phthalide-3-carboxylic acid (**8**) were synthesized by the methods of Friedlander and Reinhardt,[22] Cleve,[23] Beckmann and Liesche[24] and Gabriel,[25] respectively. Ammonium chloride-^{15}N (99 atom%) was supplied by the British Oxygen Co., Ltd.

Synthesis of *N*,4-Dichloro-1,2-naphthoquinone 2-Imine (3)——A solution of stannous chloride (5 g) in 1 N hydrochloric acid (10 ml) was added dropwise to a suspension of 4-chloro-2-nitroso-1-naphthol[26] (1 g) in concentrated hydrochloric acid (7 ml) in an ice bath. The mixture was stirred for 30 min. The resultant precipitate, 2-amino-4-chloro-1-naphthol, was collected by filtration and used in the next reaction without further purification. 2-Amino-4-chloro-1-naphthol thus obtained was suspended in 6 N hydrochloric acid (30 ml). Sodium hypochlorite solution was added dropwise to the suspension in an ice bath until the reaction was completed. The resultant precipitate was collected by filtration, washed with water, dried and purified by column chromatography on Kieselgel 60 using chloroform. The eluates were evaporated to dryness and the residue was recrystallized from *n*-hexane to give **3** as yellow needles, mp 150 °C. *Anal.* Calcd for $C_{10}H_5Cl_2NO$: C, 53.13; H, 2.23; N, 6.20. Found: C, 53.16; H, 2.04; N, 6.30. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 7.47 (1H, s), 7.57—8.28 (4H, m). MS *m/z*: 225 (M^+).

Synthesis of *N*,2-Dichloro-1,4-naphthoquinone 4-Imine (4)——A solution of sodium nitrite (0.8 g) in water (40 ml) was added dropwise to a stirred solution of 2-chloro-1-naphthol[27] (1.8 g) in ethanol (40 ml) and 4 N sulfuric acid (40 ml) in an ice bath. The reaction mixture was diluted with water (80 ml) and stirred for 30 min. The resultant precipitate was collected by filtration, washed with water, dried and purified by column chromatography on Kieselgel 60 using benzene and ethyl acetate (5 : 1). The eluates were evaporated to dryness and the residue was recrystallized from benzene to give 2-chloro-4-nitroso-1-naphthol as pale yellow crystals, mp 185—186 °C (dec.). *Anal.* Calcd for $C_{10}H_6ClNO_2$: C, 57.85; H, 2.91; N, 6.75. Found: C, 57.92; H, 2.75; N, 6.61. 2-Chloro-4-nitroso-1-naphthol (1 g) thus obtained was suspended in concentrated hydrochloric acid (7 ml). A solution of stannous chloride (5 g) in 1 N hydrochloric acid (10 ml) was added dropwise to the suspension in an ice bath. The mixture was stirred for 30 min. The resultant precipitate, 4-amino-2-chloro-1-naphthol was collected by filtration and used in the next reaction without further purification. 4-Amino-2-chloro-1-naphthol thus obtained was suspended in 6 N hydrochloric acid (30 ml). Sodium hypochlorite solution was added dropwise to the suspension in an ice bath until the reaction was completed. The resultant precipitate was collected by filtration, washed with water, dried and purified by column chromatography on Kieselgel 60 using chloroform. The eluates were evaporated to dryness and the residue was recrystallized from methanol to give **4** as yellow needles, mp 139—140 °C. *Anal.* Calcd for $C_{10}H_5Cl_2NO$: C, 53.13; H, 2.23; N, 6.20. Found: C, 53.12; H, 2.05; N, 6.07. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 8.24 (1H, s), 7.65—8.33 (4H, m). MS *m/z*: 225 (M^+).

Synthesis of 3-Cyanochloromethylphthalide (7)——Sodium hypochlorite solution (10 mmol) was added to a solution of **6** (173 mg, 1 mmol) in 0.1 N sulfuric acid (700 ml). The mixture was allowed to stand overnight at room temperature and extracted with chloroform. The chloroform layer was dried over anhydrous sodium sulfate and evaporated to dryness. The residue was chromatographed on a column of Kieselgel 60 using chloroform. The eluates were evaporated to dryness and the residue was recrystallized from chloroform–*n*-hexane to give **7** as colorless needles, mp 106 °C. *Anal.* Calcd for $C_{10}H_6ClNO_2$: C, 57.85; H, 2.91; N, 6.75. Found: C, 58.04; H, 2.88; N, 6.69.^{1}H-NMR (270 MHz, $CDCl_3$) δ: 4.94 (1H, d, J=4.8 Hz), 5.74 (1H, d, J=4.8 Hz), 7.65—8.10 (4H, m). MS *m/z*: 207 (M^+).

Formation of Cyanogen Chloride——In a 120 ml glass vial was placed 95 ml of 0.3 M phosphate buffer (pH 5.0) containing reaction material (**1**, **2**, **3**, **4**, **5**, **6**, **7**, **10**, **11**, **12** or **13**, 10 μmol). Next, 2.0 ml of 100 μmol/ml ammonium chloride aqueous solution and 3.0 ml of 100 μmol/ml sodium hypochlorite aqueous solution were added, and the vial was sealed with a rubber cap. The reaction mixture was allowed to stand for 2 h at room temperature, then 1 ml of the head space gas was injected into the GC apparatus. The cyanogen chloride standard solution was prepared from a mixture of 90 ml of 0.3 M phosphate buffer (pH 3.0), 5 ml of 0.5% chloramine-T aqueous solution and 5 ml of 1 μmol/ml potassium cyanide aqueous solution.

Reaction of 1-Naphthol (1) with Chloramine——Sodium hypochlorite solution (15 mmol) was added to 400 ml of 0.3 M phosphate buffer (pH 5.0) containing ammonium chloride (535 mg, 10 mmol). This solution was immediately added to a stirred solution of **1** (144 mg, 1 mmol) in 100 ml of 0.3 M phosphate buffer (pH 5.0). The mixture was stirred for 3 min at room temperature and extracted with ether. The ether layer was dried over anhydrous sodium sulfate and

evaporated to dryness. The residue was chromatographed on a column of Kieselgel 60 to give **4**, **5**, **3** and **2** successively from the fractions eluted with *n*-hexane–ethyl acetate (10 : 1). Compounds **4** and **5** were recrystallized from methanol and compounds **3** and **2** were recrystallized from *n*-hexane. These products (**2**—**5**) were identified by comparison with authentic samples.

Reaction of 2 with Chloramine——Sodium hypochlorite solution (6 mmol) was added to a stirred solution of **2** (76 mg, 0.4 mmol) and ammonium chloride (214 mg, 4 mmol) in 500 ml of 0.3 M phosphate buffer (pH 5.0). The reaction mixture was allowed to stand for 1 h at room temperature, acidified to pH 2 with phosphoric acid and extracted with ethyl acetate. The ethyl acetate layer was dried over anhydrous sodium sulfate and evaporated to dryness. The residue was chromatographed on a column of Kieselgel 60 using benzene–methanol–acetic acid (10 : 0.1 : 0.1). The eluates were evaporated to dryness and the residue was recrystallized from benzene to give **6**. The product (**6**) was identified by comparison with an authentic sample.

Reaction of 6 with Chloramine——Sodium hypochlorite solution (45 mmol) was added to a stirred solution of **6** (173 mg, 1 mmol) and ammonium chloride (1605 mg, 30mmol) in 1.5 l of 0.05 M phosphate buffer (pH 5.0). The reaction mixture was allowed to stand for 2 h at room temperature, concentrated to about 150 ml, acidified to pH 2 with phosphoric acid and extracted with ethyl acetate. The ethyl acetate layer was dried over anhydrous sodium sulfate and evaporated to dryness. The residue was chromatographed on a column of Kieselgel 60. The first fraction eluted with chloroform gave **7**, which was recrystallized from chloroform–*n*-hexane. The second fraction eluted with benzene–dioxane–acetic acid (10 : 1 : 1) gave **8**, which was recrystallized from benzene. The products (**7** and **8**) were identified by comparison with authentic samples.

Identification of $C^{14}NCl$ or $C^{15}NCl$——A mixture of 83.5 ml of 0.3 M phosphate buffer (pH 5.0), 3 ml of 10 μmol/ml 4-methylimidazole (**11**) or 2-methylimidazole (**13**), 4.5 ml of 100 μmol/ml ammonium chloride-^{15}N aqueous solution and 9 ml of 100 μmol/ml sodium hypochlorite aqueous solution in a 120 ml glass vial with a rubber cap was allowed to stand for 2 h at room temperature and 1 ml of the head space gas was injected into the GC-MS apparatus.

Formation of Benzonitrile (14), Benzoylformic Acid (22) and Benzoic Acid (23)——4-Phenylimidazole (**10**, 58 mg, 0.4 mmol) and ammonium chloride (321 mg, 6 mmol) were dissolved in 200 ml of 0.3 M phosphate buffer (pH 5.0). Sodium hypochlorite solution (12 mmol) was added to the solution and the reaction mixture was allowed to stand for 1 h at room temperature. A half of the reaction mixture was extracted with 10 ml of chloroform. The chloroform layer was dried over anhydrous sodium sulfate, and then subjected to GC-MS analysis for the identification of benzonitrile (**14**). The remaining reaction mixture was acidified to pH 2 with phosphoric acid and extracted with 30 ml of ethyl acetate. The ethyl acetate layer was dried over anhydrous sodium sulfate and evaporated to dryness. The residue was treated with ethereal diazomethane. The resulting solution was concentrated, and the residue was dissolved in 10 ml of chloroform. The chloroform solution was subjected to GC-MS analysis for the identification of methyl benzoylformate and methyl benzoate.

Formation of 5-Acetylamino-4-phenylimidazole (15)——Sodium hypochlorite solution (64 mmol) was added to 400 ml of 0.3 M phosphate buffer (pH 5.0) containing ammonium chloride (1.71 g, 32 mmol). This solution was immediately added to a stirred solution of 4-phenylimidazole (**10**) (576 mg, 4 mmol) in 600 ml of 0.3 M phosphate buffer (pH 5.0). The mixture was stirred for 3 min at room temperature and extracted with 150 ml of ethyl acetate. The ethyl acetate layer was dried over anhydrous sodium sulfate, then acetic anhydride (40 ml), zinc powder (6 g), acetic acid (4 ml) and sodium acetate hydrate (3 g) were added. The mixture was heated at about 80 °C for 1 h under stirring, then cooled to room temperature and filtered. The filtrate was concentrated and the residue was suspended in water (200 ml) and extracted with ethyl acetate (100 ml). The ethyl acetate layer was dried over anhydrous sodium sulfate and concentrated. The residue was chromatographed on a column of Kieselgel 60 using chloroform–methanol (10 : 3). The eluates were concentrated and the residue was chromatographed again on a column of Kieselgel 60 using benzene–methanol (10 : 3). The eluates were concentrated and the residue was crystallized from methanol–benzene to give 5-acetylamino-4-phenylimidazole (**15**) as colorless needles, mp 251—252 °C. ^{1}H-NMR (270 MHz, DCl + D_2O) δ: 2.25 (3H, s, $-COCH_3$), 7.55—7.70 (5H, m, ArH), 8.73 (1H, s, C-2-H). MS *m/z*: 201 (M^+). High-resolution MS *m/z*: 201.0901 Calcd for $C_{11}H_{11}N_3O$ (M^+). Found: *m/z* 201.0906.

Results and Discussion

Pathway of Cyanogen Chloride Formation from 1-Naphthol (1)

The reaction of 1-naphthol (**1**) with chloramine gave four products, which were identified as *N*-chloro-1,2-naphthoquinone 2-imine (**2**), *N*,4-dichloro-1,2-naphthoquinone 2-imine (**3**), *N*,2-dichloro-1,4-naphthoquinone 4-imine (**4**), and 2-chloro-1,4-naphthoquinone (**5**). These four products reacted with chloramine to give cyanogen chloride, the yields of which are shown in Fig. 1. Of these compounds, **2** and **3** gave greater amounts of cyanogen chloride than **1** did. Therefore, **2** and **3** were considered to be intermediates in the reaction.

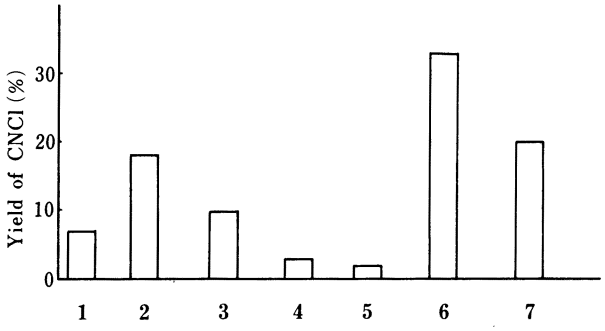

Fig. 1. Yields of Cyanogen Chloride (μmol of Cyanogen Chloride/μmol of Substrate) from Compounds **1**—**7**

Compounds **1**—**7**, 10 μmol; NH_4Cl, 200 μmol; NaClO (aqueous), 300 μmol; phosphate buffer (pH 5.0), 100 ml.

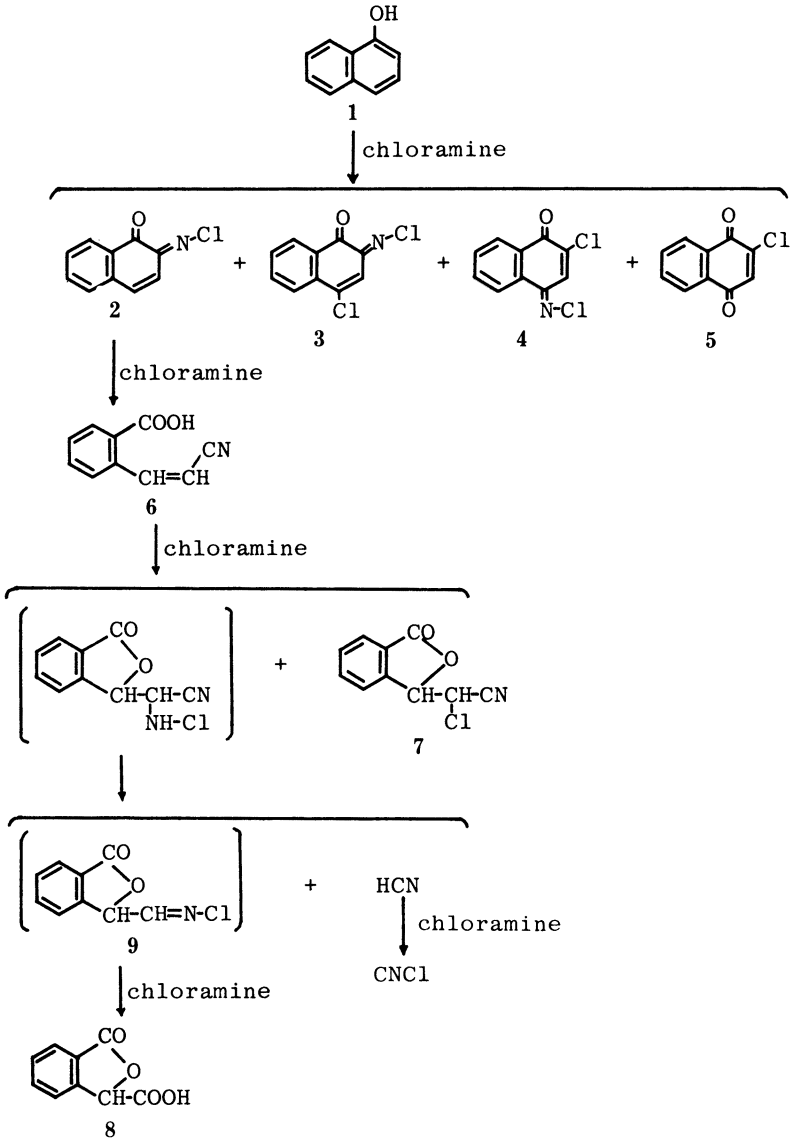

Chart 1

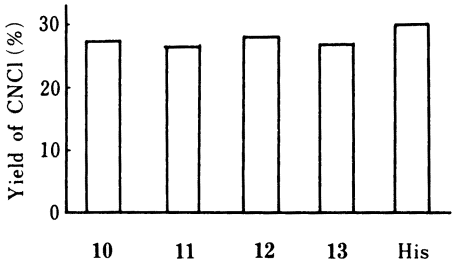

Fig. 2. Yields of Cyanogen Chloride (μmol of Cyanogen Chloride/μmol of Substrate) from Imidazole Derivatives

Imidazole derivatives, 10 μmol; NH_4Cl, 150 μmol; NaClO (aqueous), 300 μmol; phosphate buffer (pH 5.0), 100 ml.

TABLE I. Ratios of $C^{14}NCl$ and $C^{15}NCl$ to Total Cyanogen Chloride

Material	$C^{14}NCl$ (%)	$C^{15}NCl$ (%)
4-Methylimidazole (**11**)	93	7
2-Methylimidazole (**13**)	90	10

11 **13**

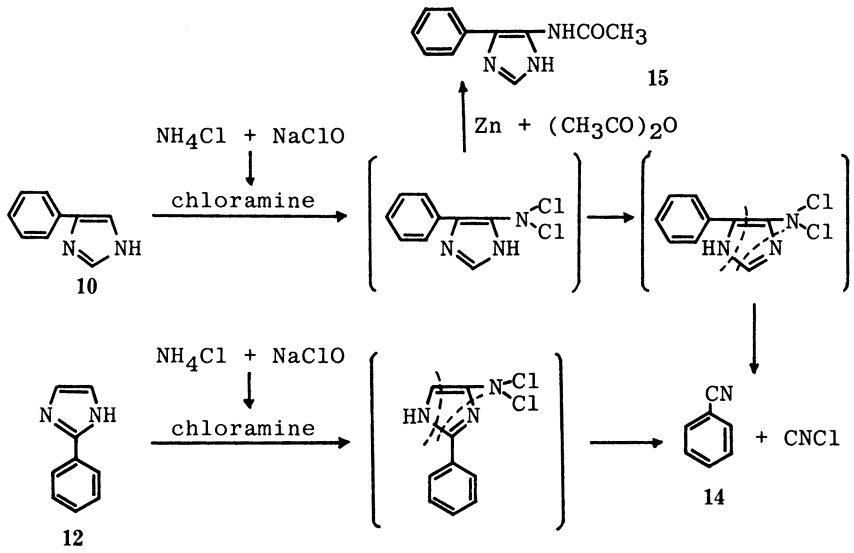

Chart 2

Further, compound **2**, which gave the highest yield of cyanogen chloride, reacted with chloramine to give *o*-carboxycinnamonitrile (**6**). The yield of cyanogen chloride from **6** was higher than that from **2** (Fig. 1). Therefore, it was concluded that **6** was an intermediate in the next reaction step.

Further, the reaction of **6** with chloramine resulted in 3-cyanochloromethylphthalide (**7**) and phthalide-3-carboxylic acid (**8**). The yield of cyanogen chloride from **7** was lower than that from **6** (Fig. 1). Therefore, **7** was not a main intermediate in the reaction.

On the basis of these results, the formation of cyanogen chloride from 1-naphthol (**1**) is considered to occur through the following steps; first, the formation of **2**, second, the conversion of **2** to **6**, third, the chloramination of **6**, then the decomposition into cyanogen

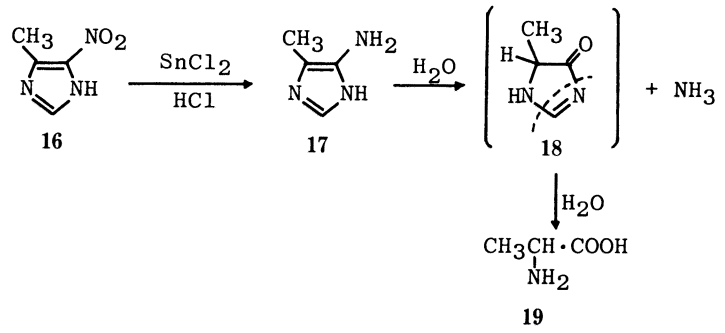

Chart 3

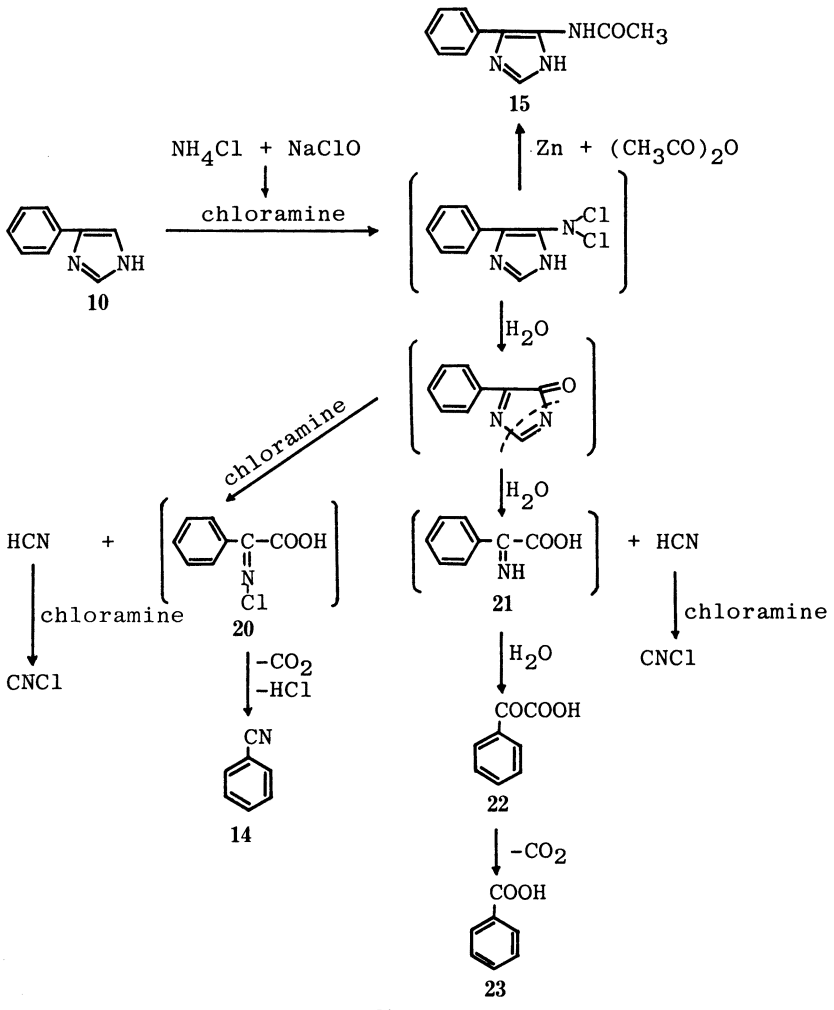

Chart 4

chloride and **9**. Compound **9** was finally converted to **8** (Chart 1).

Pathway of Cyanogen Chloride Formation from 4-Phenylimidazole (10)

4-Methylimidazole (**11**), 2-phenylimidazole (**12**) and 2-methylimidazole (**13**) besides 4-phenylimidazole (**10**) were reacted with chloramine in order to elucidate the pathway of

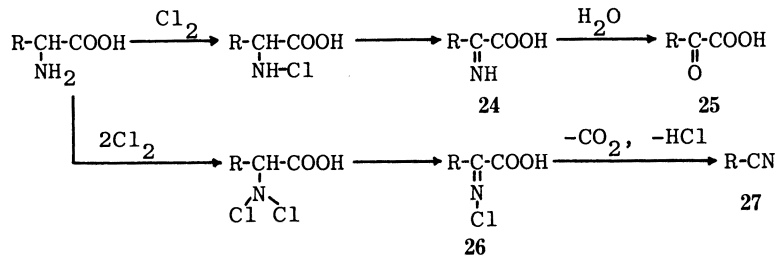

Chart 5

cyanogen chloride formation. These four imidazole derivatives gave cyanogen chloride, as did histidine (His). The yields of cyanogen chloride are shown in Fig. 2.

Then, the reactions of 4-methylimidazole (**11**) and 2-methylimidazole (**13**) with [^{15}N]-chloramine were carried out in order to clarify the origin of the nitrogen atom of cyanogen chloride (from methylimidazole or from chloramine). The resulting $C^{14}NCl$ and $C^{15}NCl$ were determined by GC-MS. The results are shown in Table I. In both cases, the nitrogen atom of cyanogen chloride originated mostly from the imidazole ring.

Further, it was found that the reaction of 4-phenylimidazole (**10**) with chloramine gave benzonitrile (**14**). 2-Phenylimidazole (**12**) also gave the same result. In addition, when the ethyl acetate extract of the reaction mixture of 4-phenylimidazole (**10**) with chloramine was treated with zinc powder and acetic anhydride, 5-acetylamino-4-phenylimidazole (**15**) was obtained; this shows that chloramine attacks the C-5 position of the imidazole ring (Chart 2).

Fargher[28] reported that the reduction of 4-methyl-5-nitroimidazole (**16**) gave alanine (**19**) and ammonia *via* 5-amino-4-methylimidazole (**17**) and 4,5-dihydro-5-methyl-4-imidazolone (**18**) (Chart 3); this shows the instability of 5-aminoimidazole derivatives.

These results indicate that chloramination occurred at the C-5 position of the imidazole ring and then the ring was cleaved along the dotted lines shown in Chart 2.

Besides the products mentioned above, benzoylformic acid (**22**) and benzoic acid (**23**) were also obtained by the reaction of 4-phenylimidazole (**10**) with chloramine.

On the basis of these results, the pathway of cyanogen chloride formation from 4-phenylimidazole (**10**) is concluded to be as shown in Chart 4; first, chloramination at the C-5 position of 4-phenylimidazole (**10**), second, the cleavage of the imidazole ring and third, the formation of cyanogen chloride, benzonitrile (**14**), benzoylformic acid (**22**) and benzoic acid (**23**). Benzonitrile (**14**) and benzoylformic acid (**22**) might be formed *via* imino intermediates (**20**, **21**); this could be explained in terms of the reaction of α-amino acid with chlorine,[29-31] in which α-keto acid (**25**) and nitrile are formed *via* imino intermediates (**24**, **26**) (Chart 5).

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