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Mechanism of Color Reaction of Aromatic Secondary and Tertiary Amines with Quinonedichlorodiimide[1]

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Quinonedichlorodiimide (I) reacts with aromatic secondary and tertiary amines to yield green colored compounds. The chemical structure of these colored compounds is investigated from the spectral data (infrared, ultraviolet, nuclear magnetic resonance, mass) and the chemical reactions.

The color of the reaction product of I and N-ethyl-*m*-toluidine (II) or N,N-diethyl-*m*-toluidine (III) is changed mutually between green and violet by oxidation and reduction.

These results and the spectral data suggest that these reactions are electrophilic displacement reactions in the *ortho* or *para* position of the alkylamino group and I reacts with II or III at the rate of 1 : 2.

Keywords——aromatic secondary amine; aromatic tertiary amine; quinonedichlorodiimide, reaction with amines; mechanism of color reaction; NMR spectra, reaction products of quinonedichlorodiimide and amines; IR spectra, reaction products of quinonedichlorodiimide and amines; mass spectra, reaction products of quinonedichlorodiimide and amines

Introduction

In the preceding paper,[3] it was reported that quinonedichlorodiimide reacts with aromatic secondary amines or tertiary amines to develop green color ($\lambda_{\max}^{\mathrm{EtOH}}$ 689 nm) on heating in the presence of potassium hydrogenphthalate, and this color reaction is applicable to the determination of such amines.

In the present paper, the chemical structure of the colored compound is investigated on the basis of the spectral data (infrared, ultraviolet, nuclear magnetic resonance and mass spectrum) and the results of the elemental analysis.

Experimental

The infrared spectra were measured in KBr disc using a Hitachi-215 spectrometer and the ultraviolet spectra were measured on a Hitachi-124 spectrophotometer. The NMR spectra were taken on a Varian HA-100 and on a Nihon denshi INN-MH-100 spectrometer in CD_3OD or $CDCl_3$ solution using TMS as an internal reference. The mass spectra were taken on a Hitachi RMU 6C and on a Nihon denshi JMS-01SG2.

Preparation of Quinonedichlorodiimide (I)——Solution A: 4% aqueous solution of sodium hypochlorite. Solution B: Concentrated hydrochloric acid (23 ml) was added to a water solution (207 ml) of *p*-phenylenediamine hydrochloride (11 g).

A solution B (230 ml) was added dropwise with stirring to a solution A (500 g) at 0°. The precipitate formed was filtered by suction and washed with H_2O. By recrystallization from 70% EtOH and then from absolute EtOH, yellow-tinged white needles were obtained, mp 126° (decomp). IR cm^{-1} (KBr): 1535 and 1565 (C=C, C=N), 840 (N-Cl). Mass Spectrum *m/e*: 174 (M^+). *Anal.* Calcd. for $C_6H_4Cl_2N_2$: C, 41.14; H, 2.29; Cl, 40.57; N, 16.00. Found: C, 41.03; H, 2.37; Cl, 40.44; N, 15.98.

Preparation of the Product (IIa)——An aqueous solution (60 ml) of potassium hydrogenphthalate (0.6 g) was added to the mixture of I (160 mg) and N-ethyl-*m*-toluidine (II) (80 mg) in EtOH (88 ml). The mixture

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[3] T. Uno and M. Yamamoto, *Bunseki kagaku*, **17**, 306 (1968).

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was refluxed on a water bath at 95° for 11 min. After cooling, the product was extracted three times with each 60 ml of ethyl acetate, and the solvent was removed under reduced pressure. The residue was dissolved in EtOH (50 ml) and was chromatographed three times on Sephadex LH-20. The green ethanolic eluate was collected. After evaporation of the solvent, a green amorphous product obtained gave a single spot on a TLC-plate. Immediate color changes of the product occurred from green to violet at room temperature by the addition of $NaHSO_3$ (5%), and violet to green at 50° by the addition of H_2O_2 (10%). Beilstain test: negative. UV λ_{max}^{EtOH} 255, 287 and 310 nm. IR cm^{-1} (KBr): 1600, 1560 and 1505 (C=C, C=N), 1280 (C–N), 1240, 1145, 1075, 1030, 860 and 810 (substituted benzene). NMR δ (CD_3OD): 1.18—1.23 (6H, triplet, N–$CH_2 \cdot C\underline{H}_3$), 3.00—3.20 (4H, quartet, N–$C\underline{H}_2 \cdot CH_3$), 2.23 (6H, singlet, –$CH_3$), 6.46—7.10 (4H, multiplet, benzene ring). Mass Spectrum *m/e*: 374 (M^+). *Anal.* Calcd. for $C_{24}H_{30}N_4$: C, 76.97; H, 8.07; N, 14.96. Found: C, 76.69; H, 7.96; N, 15.08.

Preparation of the Product (IIIa)——A solution of potassium hydrogenphthalate (0.6 g) in water (60 ml) was added to a solution of I (160 mg) and N,N-diethyl-*m*-toluidine (III) (80 mg) in EtOH (88 ml). The mixture was refluxed on a water bath at 95° for 15 min. The product (IIIa) was chromatographed and purified in the same manner as given for IIa: a green amorphous product. The color of the product (IIIa) changed by the same way as in the case of IIa. Beilstain test: negative. IR cm^{-1} (KBr): 1580 (C=C, C=N), 1320 (tertiary amine), 1245, 1150, 1110, 1065, 980 and 860 (substituted benzene). NMR δ ($CDCl_3$): 1.05—1.20 (12H, triplet, $N(CH_2 \cdot C\underline{H}_3)_2$), 3.25—3.50 (8H, quartet, $N(C\underline{H}_2 \cdot CH_3)_2$), 2.50 (6H, singlet, –$CH_3$), 7.50—7.96 (4H, multiplet, benzene ring). High resolution mass spectrum *m/e*: 430.3142. $C_{28}H_{38}N_4$ (M^+).

Results and Discussion

The color of the products (IIa and IIIa) changed alternatively between green and violet by oxidation and reduction, respectively. This result suggests that the green product is oxidized form and the violet product is reduced form.

The color compounds (IIa and IIIa) showed negative Beilstain test, indicating that the two chlorines of I were lost by the reaction.

Aromatic secondary amine having a substituent at *ortho* or *para* position reacted with I to produce colored compounds, whereas aromatic tertiary amines (*e.g.* N,N-dimethyl-*p*-toluidine) showed poor reactivity one hundredth as compared with tertiary amines having no substituent, and further N,N-diethyl-*p*-toluidine did not react.

These results suggest that these reactions are electrophilic displacement reactions in the *ortho* or *para* position of the alkylamino group. It is by the steric hindrance of the *ortho* effect that N,N-diethyl-*p*-toluidine shows the large decrease in reactivity at the *ortho* position compared with N,N-dimethyl-*p*-toluidine.

The mass spectrum of IIa (reduced form) showed the molecular ion peak at *m/e* 374 and the elemental composition was found $C_{24}H_{30}N_4$ from the results of elemental analysis. Also the molecular ion peak at *m/e* 430.3142 and the elemental composition $C_{28}H_{38}N_4$ was measured by high resolution mass spectrum of IIIa.

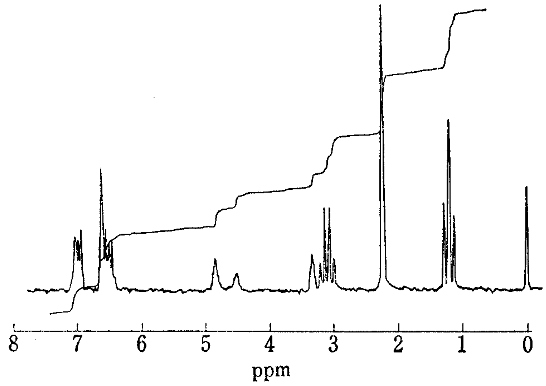

Fig. 1. NMR Spectrum of Colored Compound (IIa) (solvent: CD_3OD)

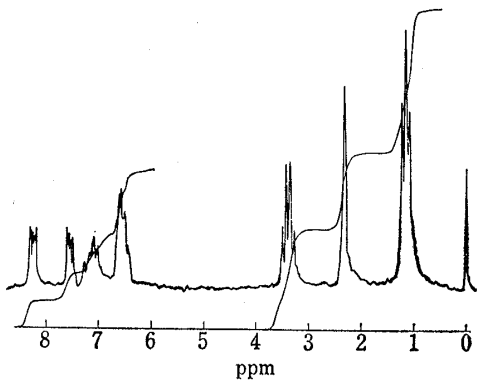

Fig. 2. NMR Spectrum of Colored Compound (IIIa) (solvent: $CDCl_3$)

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As shown in Fig. 1, IIa showed the nuclear magnetic resonance (NMR) signals for two ethyl groups having six and four hydrogens (δ 1.18—1.23, 6H triplet and δ 3.00—3.20, 4H quartet), two methyl groups (δ 2.23, 6H singlet) and for the four protons of the benzene ring (δ 6.46—7.10, 4H). As shown in Fig. 2, IIIa showed the NMR signals for four ethyl groups, two methyl groups and the benzene ring having four hydrogens.

The IR spectra of IIa exhibited strong bands due to conjugated C=C and C=N double bonds (1505, 1560 and 1600 cm^{-1}) and C–N bond in secondary amino group (1280 cm^{-1}). The broad band at 2900 cm^{-1} and the bands between 1000 and 1200 cm^{-1} were assignable to C–H stretching vibration in N-methyl group and to the substituted benzene, respectively. The IR spectra of IIIa showed strong bands due to conjugated C=C and C=N double bonds (1580 cm^{-1}), C–N bond in tertiary amine (1320 cm^{-1}) and spectra for the substituted benzene in the frequency region between 1000 and 1240 cm^{-1}.

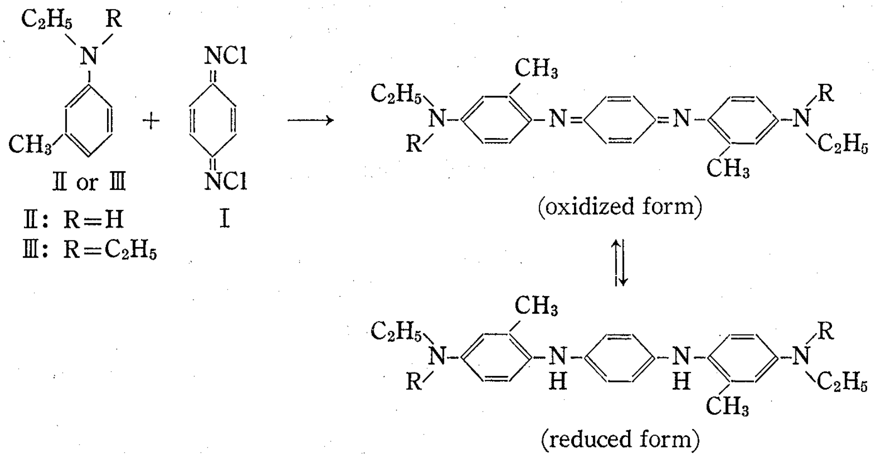

Chart 1

From the above results and the spectral data, it was concluded that I reacted with II or III at the rate of 1: 2 and the reaction mechanism was proved as shown in Chart 1.

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