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Color Reaction of Benzaldehyde with 1-Naphthol in Concentrated Sulfuric Acid

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The color reaction of benzaldehyde with 1-naphthol in concentrated sulfuric acid was investigated to clarify the reaction mechanism. Two reaction products, bis(4-hydroxy-1-naphthyl)phenylmethane and (4-hydroxy-1-naphthyl)(1-hydroxy-2-naphthyl)phenylmethane were isolated from the colored reaction mixture. These compounds were found to be the key intermediates to the colored species, since their colored solutions in concentrated sulfuric acid showed the same absorption maxima as the colored solution obtained from the reaction of benzaldehyde with 1-naphthol in the acid. The compounds were considered to be transformed into the cation radicals, which were responsible for the colorations.

Keywords——de Fazi reaction; coloration; 1-naphthol; benzaldehyde; sulfuric acid; bis(4-hydroxy-1-naphthyl)phenylmethane; (4-hydroxy-1-naphthyl)(1-hydroxy-2-naphthyl)phenylmethane; cation radical; ESR spectrum; *g* value

The condensation of benzaldehyde with an aromatic compound having a hydroxy or amino substituent group is well-known as the Baeyer[1] synthesis of triphenylmethane coloring matter. As described in the previous report,[2] we took up the reaction of de Fazi[3] as a special case of the reaction of Baeyer, and in particular investigated the mechanism of the blue coloration of benzaldehyde with acenaphthene in concentrated sulfuric acid, which shows an absorption maximum near 590 nm. We suggested that the blue-colored species of this reaction was α-(5-acenaphthenyl)benzyl cation (I), derived from bis[(5-acenaphthenyl)benzyl]ether (II) in concentrated sulfuric acid as shown in Chart 1. In connection with this work, we investigated the use of 1-naphthol in lieu of acenaphthene in concentrated sulfuric acid. Thus, the coloration of benzaldehyde with 1-naphthol in concentrated sulfuric acid was examined to elucidate the coloration mechanism, and it was found that the coloration with 1-naphthol was different from that with acenaphthene, suggesting that the reactions and coloraiton mechanisms were not the same. This paper describes the coloration mechanism of benzaldehyde with 1-naphthol in concentrated sulfuric acid. Although the reactions of 1-naphthol with aldehydes have been studied by many workers, the coloration mechanism has not previously been fully clarified.

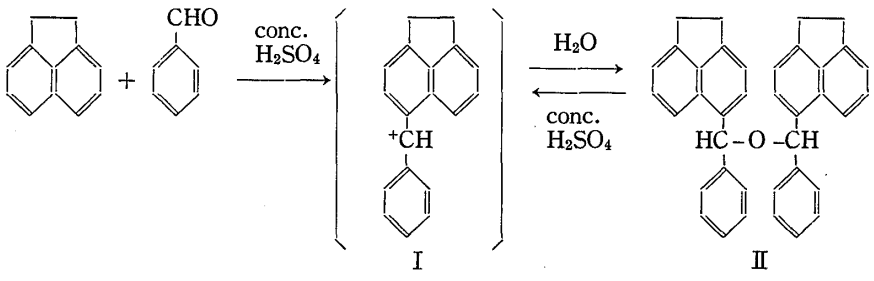

Chart 1

The reaction of benzaldehyde with 1-naphthol in concentrated sulfuric acid gave a red-colored solution with absorption maxima at 430 and 503 nm as shown in Fig. 1, (C). The red-colored reaction mixture obtained from benzaldehyde with 1-naphthol in concentrated

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sulfuric acid was poured onto crushed ice, and the reaction products were extracted with chloroform. After removal of the solvent by evaporation, the crude products were obtained. Thin-layer chromatography (TLC) was conducted on silica gel plates with chloroform: methanol=30:1 (v/v) and two spots, III (*Rf* 0.16) and IV (*Rf* 0.40), which turned red on being sprayed with concentrated sulfuric acid at room temperature, were found. The two compounds III and IV were isolated as colorless powders by column chromatography, and their structures were investigated. The molecular formula of III and IV were the same, and were established as $C_{27}H_{20}O_2$ by high resolution mass spectrometry. Their nuclear magnetic resonance (^{1}H-NMR) spectra were examined; the spectrum of III exhibited only one singlet signal for O–H protons at δ 9.90 ppm, indicating a symmetrical structure, while the spectrum of IV showed two singlet signals for O–H protons at δ 9.90 and 9.36 ppm, proving the asymmetrical structure for IV. The signals for H(9) protons were observed near δ 6.70—6.76 ppm in both compounds III and IV as shown in Fig. 2 and 3. As described above, the structures of compounds III and IV can be assigned as bis(4-hydroxy-1-naphthyl)phenylmethane and (4-hydroxy-1-naphthyl)(1-hydroxy-2-naphthyl)phenylmethane as shown in Chart 3, respectively. Infrared (IR) spectra of III and IV are also shown in Fig. 4.

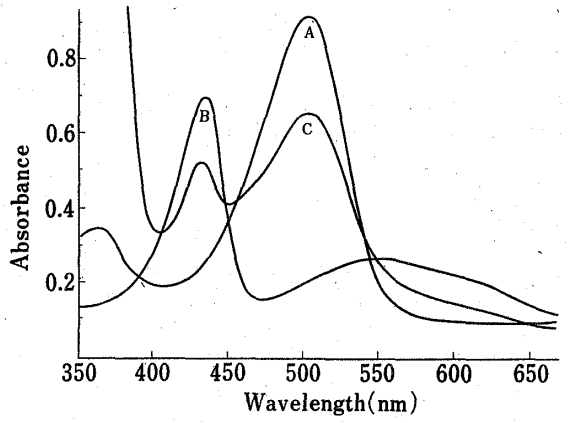

Fig. 1. Absorption Spectra of Colored Solutions of III (A), IV (B), and Benzaldehyde with 1-Naphthol (C) in conc. H_2SO_4

In order to prove that III and IV were the true mediators of the red coloration, they were dissolved in concentrated sulfuric acid and found to form a red solution immediately. The colored solutions exhibited absorption maxima at 503 and 430 nm, respectively, which coincided with those of the colored solutions produced by reacting benzaldehyde with 1-

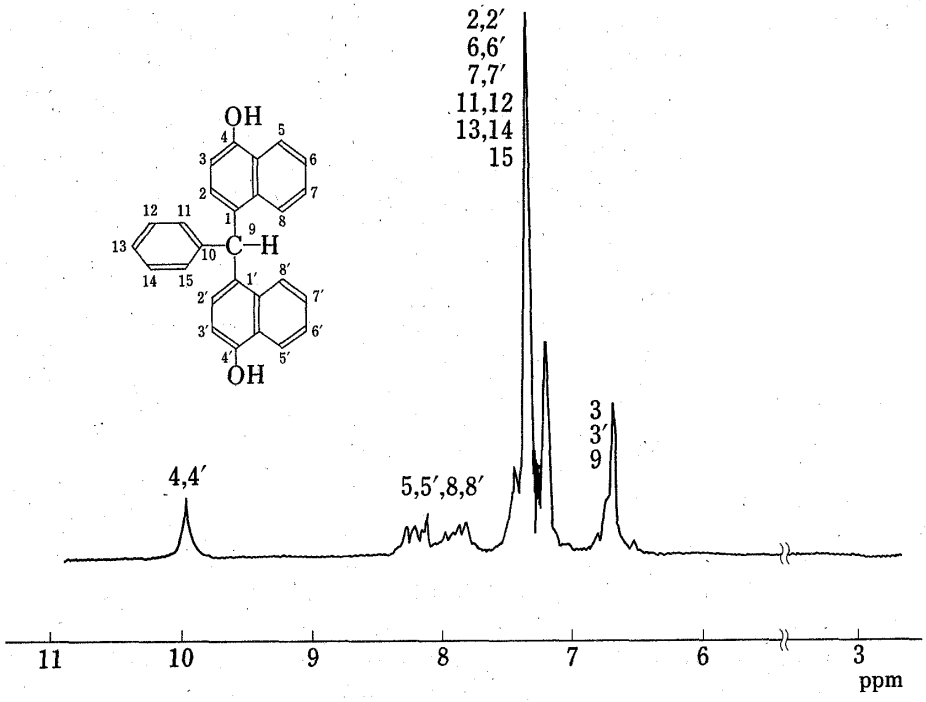

Fig. 2. ^{1}H-NMR Spectrum of III in DMSO-d_6

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naphthol in concentrated sulfuric acid (Fig. 1). Thus, III and IV were demonstrated to be closely related to the colored species.

As regards the contributions of III and IV to the coloration, the possible structures involved may be as follows: (1) carbonium cation, and/or (2) quinoid form, and/or (3) free radical. Bredereck claimed that a colored quinoid form was afforded by the reaction of

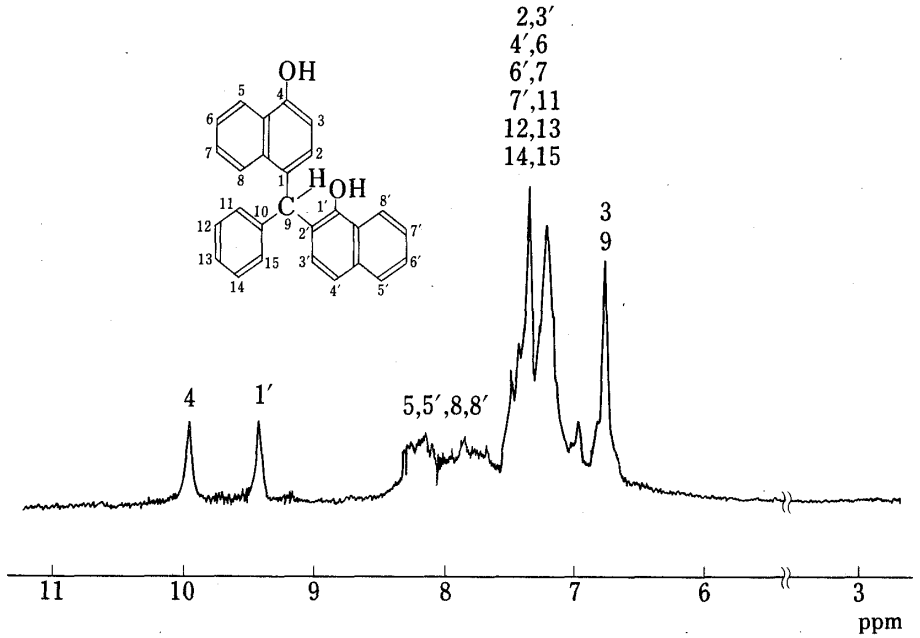

Fig. 3. ^{1}H-NMR Spectrum of IV in DMSO-d_6

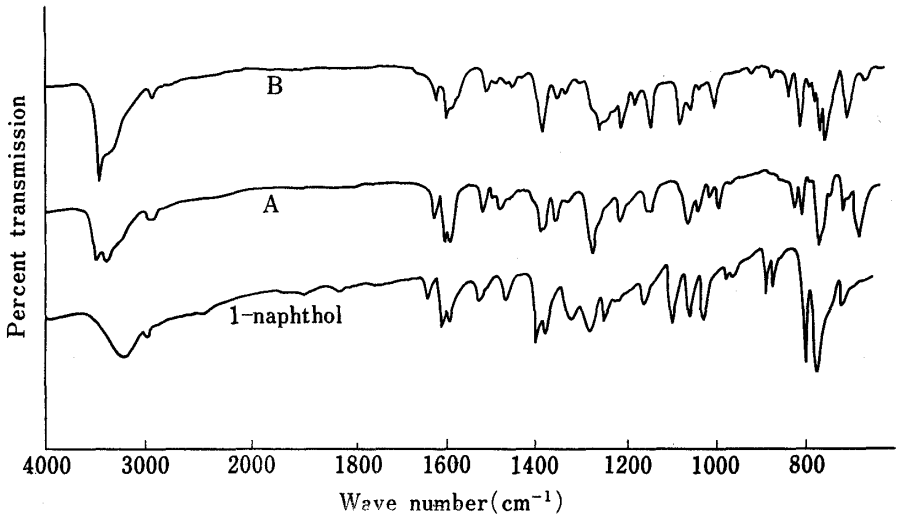

Fig. 4. IR Spectra of III (A), IV (B), and 1-Naphthol (in KBr)

V: R=1-(4-hydroxynaphthyl) VII: R=1-(4-hydroxynaphthyl)
VI: R=2-(1-hydroxynaphthyl) VIII: R=2-(1-hydroxynaphthyl)

Chart 2

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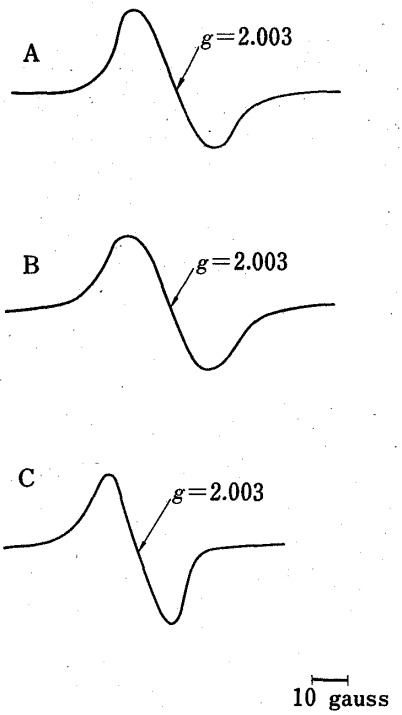

Fig. 5. ESR Spectra of the Free Radicals detected in the Colored Solutions of III (A), IV (B), and Benzaldehyde with 1-Naphthol (C) in conc. H_2SO_4

furfural with 1-naphthol.[4,5] However, this was not the case in the reaction of furfural with 1-naphthol in concentrated sulfuric acid. The conversions of III and IV to naphthoquinones V and VI, as denoted in Chart 2, were not favored for the present colored species, because the oxidation–reduction between III and V, and between IV and VI was not reversible in the concentrated sulfuric acid and water media. Compounds III and IV were formed in the reaction of benzaldehyde with 1-naphthol and gave the coloration in concentrated sulfuric acid, but were recovered as naphthol forms, not as naphthoquinone forms, on dilution with water. Therefore, quinoid formation should be excluded from the coloration mechanism. Next, the formation of carbonium cation can be considered, as shown by VII and VIII in Chart 2. However, we could not find any indication of the existence of a carbonium cation, and thus the contribution of carbonium cation to the red coloration remains unclear at present. The possible formation of free radical was next considered. In fact, the free radicals were detected in the colored solutions of benzaldehyde with 1-naphthol, III, and IV concentrated sulfuric acid by electron spin resonance (ESR) measurement. The g values of all free radicals were the same, 2.003. The ESR spectral patterns of all free radicals were similar to each other, as shown in Fig. 5. These free radicals were assumed to be cation radicals[6–9] such as IX and X, as shown in Chart 3, of the type responsible for the coloration in the condensation of benzaldehyde with 1-naphthol in concentrated sulfuric acid. Thus, the contribution of free radicals to the coloration was clearly proved.

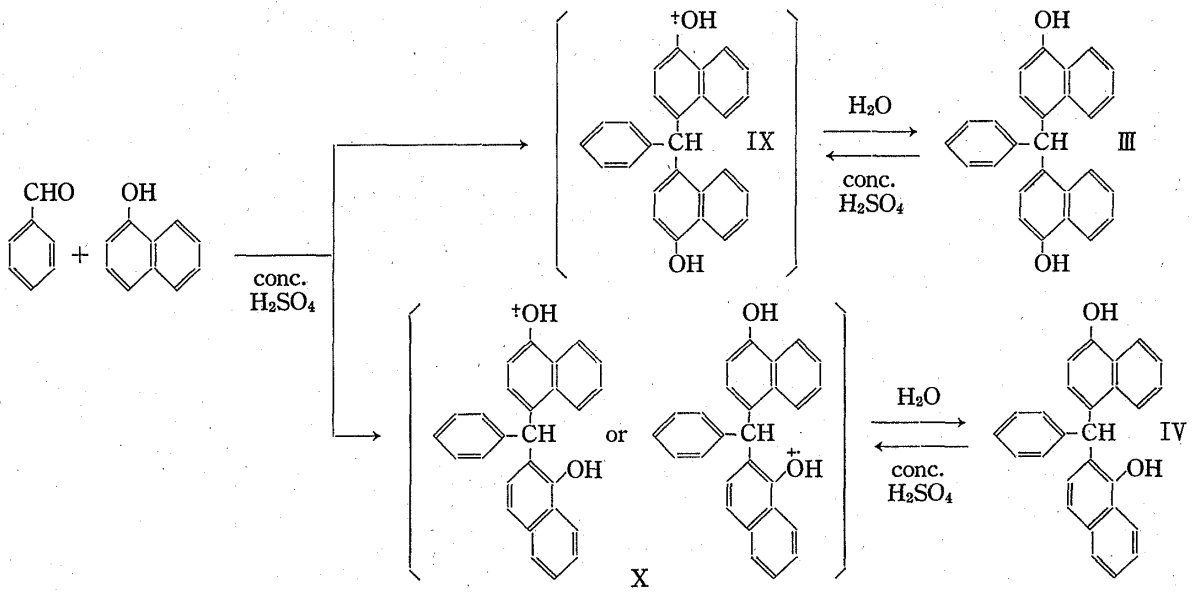

Chart 3

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As discussed above, it was found that the color reaction of benzaldehyde with 1-naphthol in concentrated sulfuric acid afforded III and IV as reaction products, and the coloration could be ascribed to the cation radicals IX and X derived from the products.

Although many triphenylmethane coloring materials have been synthesized by reactions of aldehydes with aromatic compounds, their coloration mechanisms have not previously been known. This work is the first to cast light on the problem. Further studies are in progress and the results will be reported shortly.

Experimental

Absorption spectra were measured with a Shimadzu MPS-50L spectrophotometer in a cell of 10 mm optical length, IR spectra with a JASCO IR-G spectrophotometer, ^{1}H-NMR spectra with a Varian T-60 spectrometer at 60 MHz with tetramethylsilane as an internal standard, mass spectra (MS) with a JMS-D100 mass spectrometer, and high resolution mass spectra with a JMS-01S spectrometer. ESR spectra were obtained on a JEOL JMS-ME-1X spectrometer with manganese monoxide as an external standard. Melting points were determined with a Yamato Scientific stirred liquid apparatus and are uncorrected. All *Rf* values were obtained on silica gel plates with $CHCl_3$–CH_3OH (30: 1, v/v) as the developing solvent.

Reaction of Benzaldehyde with 1-Naphthol in Concentrated Sulfuric Acid——A solution of benzaldehyde (6.7 g, 42 mmol) and 1-naphthol (4.9 g, 42 mmol) in $CHCl_3$ (300 ml) was added gradually to conc. H_2SO_4 (400 ml) at −10°C with stirring to afford a red-colored solution; stirring was continued at the same temperature for 3 h. The colored reaction mixture was poured onto crushed ice, and the reaction products were extracted with $CHCl_3$. The organic layer was washed with water and aq. satd. $NaHCO_3$, then dried over Na_2SO_4. Removal of the solvent by evaporation left a residue, which was subjected to column chromatography on silica gel. Elution with $CHCl_3$–CH_3OH (30: 1, v/v) gave benzaldehyde (*Rf* 0.75), 1-naphthol (*Rf* 0.70), compound IV (*Rf* 0.40), and compound III (*Rf* 0.16).

Bis(4-hydroxy-1-naphthyl)phenylmethane (III)——Yield, 0.45 g. Recrystallization from benzene–ligroin gave a colorless powder, mp 125°C (dec.). MS *m/e*: M^+, 376.1446. Calcd for $C_{27}H_{20}O_2$: M, 376.1463.. ^{1}H-NMR δ (DMSO-d_6): 9.90 (2H, s, O–H: 4,4′), 7.76—8.33 (4H, m, H: 5,5′, 8,8′), 7.10—7.60 (11H, m, H: 2,2′, 6,6′, 7,7′, 11, 12, 13, 14, 15), 6.70 (3H, s, H: 3, 3′, 9). VIS $\lambda_{max}^{H_2SO_4}$ nm (log ε): 5.03 (4.05).

(4-Hydroxy-1-naphthyl)(1-hydroxy-2-naphthyl)phenylmethane (IV)——Yield, 0.20 g. Recrystallization from benzene–ligroin gave a colorless powder, mp 205—206°C. MS *m/e*: M^+, 376.1460. Calcd for $C_{27}H_{20}O_2$: M, 376.1463. ^{1}H-NMR δ (DMSO-d_6): 9.90 (1H, s, O–H: 4), 9.36 (1H, s, O–H: 1′), 7.70—8.33 (4H, m, H: 5, 5′, 8, 8′), 7.06—7.60 (12H, m, H: 2, 3′, 4′, 6, 6′, 7, 7′, 11, 12, 13, 14, 15), 6.76 (2H, s, H: 3, 9). VIS $\lambda_{max}^{H_2SO_4}$ nm (log ε): 430 (4.81).

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References and Notes

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