[Chem. Pharm. Bull. 21(2) 383—387 (1973)]

UDC 547.678.2.04 : 547.58.26.04

Color Reaction of Aromatic Aldehydes with Acenaphthene in Concentrated Sulfuric Acid

Takeo Ueda, Atsushi Takada, and Matajiro Koyama

School of Pharmaceutical Sciences, Kitasato University[1)]

(Received August 24, 1972)

The color reaction of aromatic aldehyde with acenaphthene was investigated to clarify the mechanism of the coloration. When the colored solution of aldehyde with acenaphthene in concentrated sulfuric acid was treated with ice water, bis[1-(5-acenaphthenyl)benzyl] ether derivative was obtained, as a reaction product. It was assumed that the coloration might be ascribed to 1-(5-acenaphthenyl)benzyl cation derivative.

It was reported by de Fazi that aromatic aldehydes showed an intense blue color, when reacted with acenaphthene (AN) in concentrated sulfuric acid, but any aliphatic aldehyde did not give any characteristic coloration, even if a blackish precipitation was occasionally formed.[2)] De Fazi claimed that this coloration could be effectively used to detect aromatic aldehydes. Actually, this test was introduced in Hans Meyer's work to prove the existence of benzaldehyde.[3)] De Fazi offered the mechanism of this coloration which is shown in Chart 1.[2a)] His assumption, however, seemed to be in conflict with the modern electronic theory. It, therefore, may be said that the mechanism of this coloration has not been made clear, and neither colored substance nor reaction product associated with the coloration has not been isolated, yet. The authors isolated the reaction product of this color reaction in crystalline form and investigated the structure of this compound, together with the mechanism of the coloration.

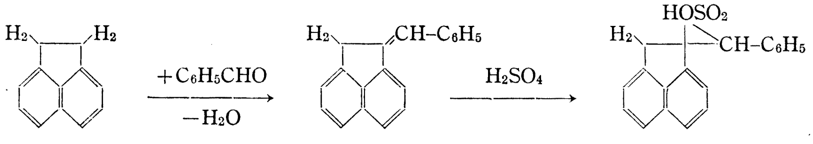


Chart 1

The reaction between benzaldehyde and AN in concentrated sulfuric acid was carried out under the condition, as described in the experimental part. The reaction mixture was poured onto crushed ice and extracted the mixture with ether. From the ether extract, colorless prisms of mp 196—197° (Ia) was obtained. The absorption maxima of the colored solution of Ia in sulfuric acid was observed at 588 nm and 383 nm, as shown in Fig. 1, and these maxima changed to 560 nm on standing for 225 minutes at room temperature. The colored solution resulted from the reaction of benzaldehyde with AN in sulfuric acid exhibited two absorption maxima at 590 nm and 458 nm. Between them, the former shifted to 560 nm after 240 minutes at room temperature, and the latter might be that of benzaldehyde in sulfuric acid, since the solution of benzaldehyde in sulfuric acid showed the absorption maximum at 460 nm. These results suggest that Ia was closely related to the colored substance produced

---

1) Location: *Shirokane, Minato-ku, Tokyo.*

2) *a)* R. de Fazi, *Gazz. Chim. Ital.*, **46, I**, 334 (1916) [*C.A.*, **11**, 1144 (1917)]; *b) Idem, ibid.*, **51, I**, 328 (1921) [*C.A.*, **16**, 79 (1922)]; *c) Idem, ibid.*, **54**, 658 (1924) [*C.A.*, **19**, 821 (1925)].

3) H. Meyer, "Nachweis und Bestimmung Organischer Verbindungen," Verlag von Julius Springer, Berlin, 1933, p. 274.

by the reaction of benzaldehyde with AN in sulfuric acid.

The molecular formula of Ia was established as $C_{38}H_{30}O$ from the molecular ion (M^+) in a high resolution mass spectrum (MS) (Calcd. 502.230, Found 502.229), which also agreed to the data of the elemental analysis. The infrared (IR) spectrum of Ia (Fig. 2) showed the presence of ethereal or alcoholic C–O by its absorption band at 1020 cm^{-1}, but not any O–H band at around 3400 cm^{-1}. Szymanski described regarding the IR spectra of methyl ether substituted with phenyl such as triphenylmethyl ether or 4-benzyloxyphenol that the ν(C–O) appeared near 1000 cm^{-1} or at a low frequency of 1020 cm^{-1} since the phenyl group could remove electron density from the C–O group.[4] This finding indicated that Ia might be a methyl ether substituted with aromatic moieties. The MS obtained also supported the ethereal structure of Ia, because an intense peak at *m/e* 259 was observed, which corresponds to $C_{19}H_{15}$-O ($M-C_{19}H_{15}$, Calcd. 259.112, Found 259.111), indicating that Ia might be $C_{19}H_{15}$-O-$C_{19}H_{15}$.

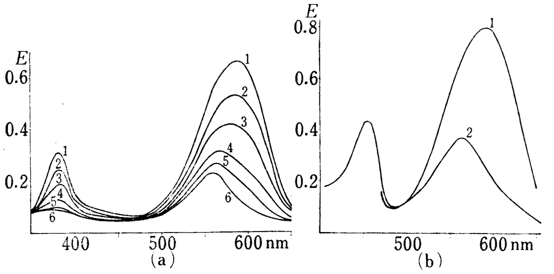


Fig. 1. Absorption Spectra of Ia in conc. H_2SO_4 (a) and Colored Solution of Benzaldehyde with AN in conc. H_2SO_4 (b)

a : 40 μg of Ia was dissolved in 10 ml of conc. H_2SO_4, kept for several periods (1—6) at room temperature. The time (min) is 1: immediately, 2: 30, 3: 60, 4: 105, 5: 165, 6: 225.
b : 275 μg of benzaldehyde and 300 μg of AN were dissolved in 10 ml of conc. H_2SO_4, kept for several periods (1—2) at room temperature. Time (min) is 1: immediately, 2: 240.

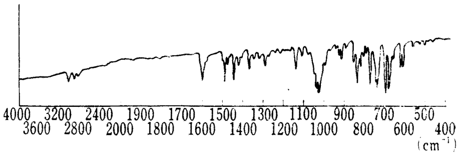


Fig. 2. IR Spectrum of Ia (in KBr)

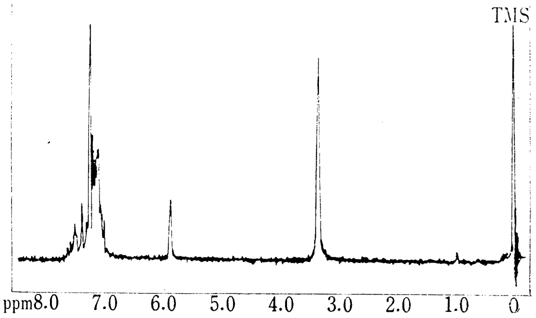


Fig. 3. NMR Spectrum of Ia in CCl_4

The nuclear magnetic resonance (NMR) spectrum of Ia was shown in Fig. 3. The signal at 3.39 ppm (singlet, 4H) was assigned to a methylene proton of peri-position on a AN ring and a multiplet at 7.34 ppm (10H) was aromatic proton on naphthalene and benzene ring. The signal at 5.90 ppm (singlet, 1H) was assigned to a methin proton, which might have no proton at viccinal carbon atoms. On the basis of the above results together with the consideration of the characteristic of AN that its 5 or 6-position is the most reactive, Ia should be bis[1-(5-acenaphthenyl)benzyl] ether.

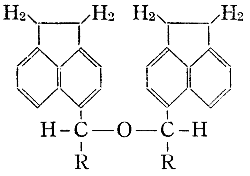
To confirm this structure, the reaction product of (5-acenaphthenyl)phenylcarbinol[5] (II) in concentrated sulfuric acid was investigated. II showed the similar coloration to that of Ia in sulfuric acid, as reported by Dziewonski,[5] and the absorption maxima of both solutions were identical. According to the similar method to the isolation of Ia, the colored solution from II in sulfuric acid was treated, and the colorless prisms of mp 195—196° was obtained which was identified with Ia by the mixing melting point test and the comparison of their IR spectra. Thus, Ia was confirmed to be bis[1-(5-acenaphthenyl)benzyl] ether, as shown in Chart 2.

---

[4] H.A. Szymanski, "Interpreted Infrared Spectra," Vol. 3, Plenum Press Data Division, New York, N.Y., 1967, p. 116; *idem*, *ibid.*, p. 151.

[5] K, Dziewonski and M. Rychlik, *Ber.*, **58**, 144 (1925).

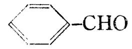
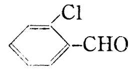
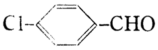
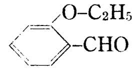
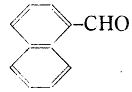
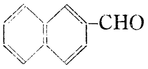
The reactions of several other aromatic aldehydes with AN in concentrated sulfuric acid were also examined, and the reaction products were isolated according to the similar method to that of Ia. The solutions of these products in concentrated sulfuric acid showed the same absorption maximum as the solution of a corresponding aromatic aldehyde with AN in sulfuric acid. The data of MS measurement, the IR spectra and the data of elemental analysis of these products coincide with the structure of bis((5-acenaphthenyl)-(substituted phenyl)methyl] ether, as shown in Table I.



Ia: R=C_6H_5, Ib: R=2-Cl-C_6H_4,
Ic: R=4-Cl-C_6H_4, Id: R=2-EtO-C_6H_4,
Ie: R=1-naphthyl, If: R=2-naphthyl

Chart 2

Table I. Reaction Product of Aromatic Aldehyde with AN in Conc. H_2SO_4

Aldehyde	Reaction product									$\lambda_{max}^{H_2SO_4}$ (nm) Aldehyde +AN
	Comp.	mp (°C)	Appearance	Formula	Mass Spectrum (M^+) m/e Calcd. (Found)	Analysis (%) Calcd. (Found) C	H	IR ν (C–O) (cm^{-1})	$\lambda_{max}^{H_2SO_4}$ (nm) (log ε)	
	Ia	196—197	prisms	$C_{38}H_{30}O$	502.230 (502.229)	90.80 (90.74)	6.02 (6.13)	1020	588 (4.92) 383	590
	Ib	249—250	plates	$C_{38}H_{28}OCl_2$	570.151 (570.149)	79.86 (79.91)	4.94 (4.94)	1030	590 (4.53) 388	590
	Ic	230—231	plates	$C_{38}H_{28}OCl_2$	570.151 (570.152)	79.86 (80.03)	4.94 (4.98)	1010	603 (4.53) 398	603
	Id	231—232	plates	$C_{42}H_{38}O_3$	590.283 (590.284)	85.39 (85.42)	6.48 (6.53)	1050	618 (5.96)	615
	Ie	87—88	plates	$C_{46}H_{34}O$	602.261 (602.262)	91.66 (91.80)	5.69 (5.47)	1050	658 (5.27)	663
	If	89—90	plates	$C_{46}H_{34}O$	602.261 (602.263)	91.66 (91.53)	5.69 (5.62)	1055	623 (5.27)	622

Some chemical behaviors of the colored solution of Ia in concentrated sulfuric acid were examined to see if the coloration mechanism could be clarified. The colored solution of Ia in sulfuric acid was treated with cold ethanol according to the method described in the experimental part. It was found by the thin-layer chromatography (TLC) that the resulting oil from Ia and ethanol was constituted from three spots. Among them, small spots at *Rf* 0.68 and 0.32 coincide in position with Ia and II by the TLC, respectively, and the main product (III) (*Rf* 0.57) was purified by column chromatography on silica gel. III was yellowish oil and shown to have molecular formula of $C_{21}H_{20}O$ by the MS measurement (M^+, Calcd. 288.151, Found 288.149). The IR spectrum of III (Fig. 4) showed the presence of ethereal C–O by its absorption band at 1090 cm^{-1}. From these results, the structure of III might be ethyl 1-(5-acenaphthenyl)benzyl ether. The solution of III in concentrated sulfuric acid showed its absorption maxima at 590 nm and 383 nm just as same as Ia in sulfuric acid, and these maxima changed to 560 nm with the elapse of time. Furthermore, it was found that III was also changed to Ia, when the colored solution of III in concentrated sulfuric acid was treated with ice water.

These findings suggest that benzaldehyde might be condensed with AN in concentrated sulfuric acid to form 1-(5-acenaphthenyl)benzyl cation (IV) at the first step, and this cation

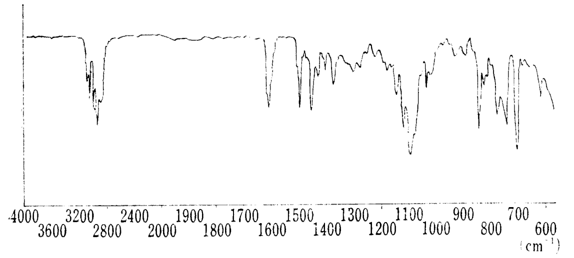


Fig. 4. IR Spectrum of III (Film)

might be also formed from I, II or III in concentrated sulfuric acid, that is, the cation IV might be formed in all of the colored solutions. Cation IV may be converted to III by the nucleophilic attack with ethanol. IV may be coverted to II with water, and then the reaction between II and IV is occured to yield I, as shown in Chart 4. On the other hand, any signal was not found in the electron spin resonance measurements of the colored solutions, indicating that this coloration was not ascribed to the formation of cation radical. From these results, it was assumed that the coloration of aromatic aldehydes with AN in sulfuric acid might be ascribed to the cation IV.

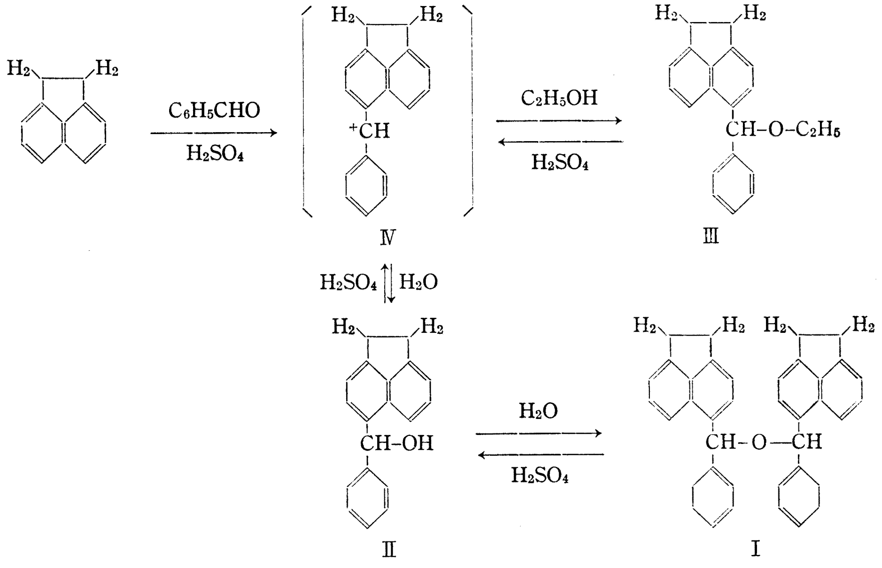


Chart 3

As described above, the authors investigated the color reaction of aromatic aldehydes with AN in concentrated sulfuric acid, and isolated bis[1-(5-acenaphthenyl)benzyl] ether, as the reaction product, when treated the colored solution with ice water. The authors assumed that this coloration might be ascribed to 1-(5-acenaphthenyl)benzyl cation derivative which was formed by the condensation of aromatic aldehyde with AN in concentrated sulfuric acid.

Experimental[6]

General Procedure for the Isolation of the Reaction Product of Aromatic Aldehyde with Acenaphthene in Concentrated Sulfuric Acid——Into 400 ml of conc. H_2SO_4 a solution of 0.026 mole of aromatic aldehyde and 4 g (0.026 mole) of AN in 300 ml of $CHCl_3$ was added gradually at $-10°$ with stirring, and the stirring and chilling were continued for 1—3 hr to complete the coloration. The colored reaction mixture was

---

[6] Absorption spectra were measured by a Shimazu MPS-50L Spectrometer in a cell of 10 mm optical length, IR spectra by Shimazu IRG-1 Spectrometer, NMR spectra by Varian T-60 Spectrometer at 60 MHz with tetramethylsilane as internal standard, and MS by JEOL JMS-01S Mass Spectrometer.

poured onto crushed ice, extracted with ether, washed with water and aq. satd. $NaHCO_3$ successively, and dried over Na_2SO_4. After removal of ether by evaporation, the residue was treated with ligroin to remove unreacted aldehyde, and the separated precipitate was collected by suction. If aldehyde could not be removed enough by this treatment, the residual oil was dissolved in 100 ml of ether, washed with aq. satd. $NaHSO_3$, dried over Na_2SO_4, and evaporated to dryness. The residue was purified by column chromatography on silica gel. Elution with benzene gave a crude product.

Reaction Product of Benzaldehyde with Acenaphthene (Ia)——Yield of crude product, 1.3 g. Recrystallization from benzene gave 200 mg of colorless prisms, mp 196—197°.

Reaction Product of 2-Chlorobenzaldehyde with Acenaphthene (Ib)——Yield of the crude product, 1.5 g. Recrystallization from benzene gave 800 mg of colorless plates, mp 249—250°.

Reaction Product of 4-Chlorobenzaldehyde with Acenaphthene (Ic)——Yield of crude product, 1.5 g. Recrystallization from benzene gave 300 mg of colorless plates, mp 230—231°.

Reaction Product of 2-Ethoxybenzaldehyde with Acenaphthene (Id)——Yield of the crude product, 0.1 g. Recrystallization from MeOH gave 10 mg of colorless plates, mp 231—232°.

Reaction Product of 1-Naphthaldehyde with Acenaphthene (Ie)——Yield of the crude product, 0.1 g. Recrystallization from ligroine–MeOH gave 20 mg of colorless plates, mp 87—88°.

Reaction Product of 2-Naphthaldehyde with Acenaphthene (If)——Yield of the crude product, 0.2 g. Recrystallization from ligroine–MeOH gave colorless plates, mp 89—90°.

Isolation of the Reaction Product of (5-Acenaphthenyl)phenylcarbinol (II) in Concentrated Sulfuric Acid Into a solution of 1 g of II in 100 ml of $CHCl_3$, 100 ml of conc. H_2SO_4 was added with strring under chilling at −10°, and the stirring and the chilling were continued for 1 hr to complete the coloration. The colored solution was poured onto crushed ice, extracted with ether, washed with aq. stad. $NaHCO_3$, and dried over Na_2SO_4. After evaporating ether, 0.9 g of the crude product was obtained and recrystallized from a small amount of benzene to give 500 mg of colorless prisms (Ia) of mp 195—196°. *Anal.* Calcd. for $C_{38}H_{30}O$: C, 90.80; H, 6.02. Found: C, 90.83; H, 6.00. IR ν_{max}^{KBr} cm^{-1}: 1020 (C–O).

Isolation of Ethyl 1-(5-Acenaphthenyl)benzyl Ether (III)——Into a solution of 50 mg of Ia in 50 ml of $CHCl_3$, 5 ml of conc. H_2SO_4 was added at −10° with stirring, and the stirring and the chilling were continued for 1 hr to complete the coloration. The cold reaction mixture was added into 100 ml of EtOH at −10° with stirring, then, the resulting solution was poured into 1000 ml of ice water, and extracted with ether. The extract was washed with water and aq. satd. $NaHCO_3$ successively, dried over Na_2SO_4, and ether was distilled off. The residual oil was dissolved in 5 ml of benzene, adsorbed to the column packed with silica gel, and eluted with benzene. A fraction at $Rf=0.57$ in TLC (silica gel, benzene) was collected, and benzene was removed by evaporation to give 25 mg of yellowish oil.

Isolation of the Reaction Product of III in Concentrated Sulfuric Acid——Into a solution of 10 mg of III in 2 ml of $CHCl_3$, 2 ml of conc. H_2SO_4 was added at −10° and stood for 1 hr. The colored solution was poured onto crushed ice and treated by the similar way described above. After evaporation of ether, the residue was purified by column chromatography on silica gel. Elution with benzene gave 7 mg of oily product. This oil gave single spot at $Rf=0.68$ in TLC (silica gel, benzene) which coincide in position with Ia. IR ν_{max}^{Film} cm^{-1}: 1020 (C–O). Mass Spectrum *m/e*: 502 (M^+).