

Colored Products Formed by the Reaction of *o*-Acetylbenzophenone with Hydrazine-hydrochloride, 2-Aminoethanol and its Methylether

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The reaction of *o*-acetylbenzophenone[1] with 2-aminoethanol and its methylether gave red and deep blue pigments, respectively. The structures of these pigments were determined as follows: red pigments [2b,2c]: 1, 2-bis (2-substituted-3-phenyl-1-isoindolyl)ethylene; deep blue pigments [3b,3c]: 1,1'-disubstituted-5,5'-diphenyl-3,4 : 3',4'-dibenzo-2,2'-dipyrrromethenium chloride. 1-Hydroxyethyl-5,5'-diphenyl-3,4 : 3',4'-dibenzo-2,2'-dipyrrromethene [5b] was prepared and its structure was determined by comparison with that of [3b].

[1] reacted with hydrazine-hydrochloride to give 1-methyl-4-phenylphthalazine[7] as light brown pigment as well as 1-(3-phenyl-1-isoindolylidene) methyl-4-phenylphthalazine hydrochloride [6] and [5a] as deep blue pigments. From [7] and 4-phenyl-1-phthalazinecarbaldehyde, [8] was synthesized and its properties were examined in connection with [7] and [2].

o-Acetylbenzophenone [1] reacted with various primary amines in the presence of acetic acid and/or hydrochloric acid to give violet reaction mixtures. From these reaction mixtures, one type of red and three types of deep blue pigments had been isolated and their structures were determined by the authors previously.¹⁾

This paper describes the structures of the colored products formed by the reactions of [1] with hydrazine-hydrochloride, 2-aminoethanol and its methylether in connection with the pigments investigated previously.

Reactions of o-Acetylbenzophenone [1] with 2-Aminoethanol and its Methylether

The reactions of [1] with 2-aminoethanol and its methylether gave red and deep blue pigments respectively. The structures of these pigments were analogous to those of corresponding pigments from [1] and various primary amines, as red pigments: 1, 2-bis(2-substituted-3-phenyl-1-isoindolyl)ethylene [2b,2c]: and as deep blue pigments: 1, 1'-disubstituted-5,5'-diphenyl-3,4 : 3',4'-dibenzo-2,2'-dipyrrromethenium chloride [3b,3c].

In the reaction between [1] and 2-aminoethanol, another deep blue pigment was isolated. It had been

previously determined to be 1-[2-(3-phenyl-1-isobenzofuranyl)-2-(2-(2-hydroxyethyl)-3-phenyl-1-isoindolyl)ethenyl]-2-(2-hydroxyethyl)-3-phenyl-isoindole N-oxide [4b]²⁾.

1-Hydroxyethyl-5,5'-diphenyl-3,4 : 3',4'-dibenzo-2,2'-dipyrrromethene [5b] was prepared by the reaction of [1] with 1-hydroxy-3-methyl-1-phenyl-1H-isoindole and 2-aminoethanol. Then its IR, UV, NMR and mass spectra were measured to differentiate between [3b] and [5b].

The UV absorption maximum of [5b] in acidic solution was nearly equal to that of [3b] in both acidic and neutral solutions. It was suggested that the conjugated system of [5b] in acidic solution is similar to that of [3b].

Reaction of [1] with Hydrazine-hydrochloride

[1] reacted with hydrazine-hydrochloride to give one light brown and two deep blue pigments.

One of the deep blue pigments was identified as 1-(3-phenyl-1-isoindolylidene)methyl-4-phenyl-phthalazine hydrochloride [6] on the basis of its IR, UV and mass spectra, and also because of its elementary analysis and its chemical behavior.

The other deep blue pigment was found to be 5,5'-diphenyl-3,4 : 3',4'-dibenzo-2,2'-dipyrrromethene

[5a], which was the main reaction product formed by the reaction of [1] with ammonia. The formation of this [5a] was deduced from the fact that hydrazine-hydrochloride liberated ammonia in the absence of [1], under conditions similar to those of pigment formations.

The structure of the light brown pigment was identified as 1-methyl-4-phenylphthalazine [7] by comparing its IR and mass spectra and its melting point with those of the authentic sample. When [7] was recrystallized several times from a benzene-hexane solution, it became colorless.

In order to obtain information on the compound forming such an ethylene-type structure as [2], 1,2-bis(4-phenyl-1-phthalazinyl) ethylene [8] was synthesized by the reaction of [7] with 4-phenyl-1-phthalazinecarbaldehyde [9] in the presence of zinc chloride. [8] had yellowish orange color, while all of [2] were red. This is probably due to a decrease of coplanarity resulting from the close contact between

hydrogens at the ortho-position of 4-phenyl, and at the 5-position of 1-phthalazinyl of [8].

From the reaction mixture of [1] and hydrazine-hydrochloride no [8] was obtained.

Experimental

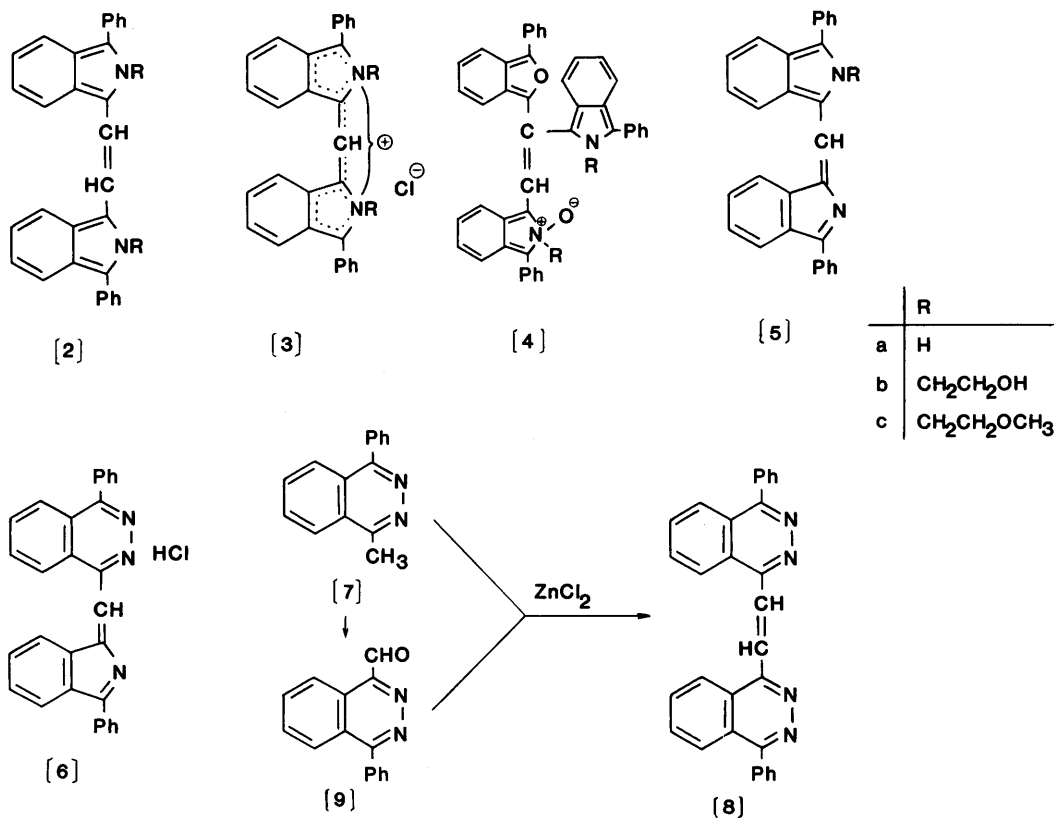
Melting points were determined on a Yanaco micro-melting point apparatus.

IR and UV spectra were recorded on a JASCO DS-701G and a JASCO UVIDE C-505 spectrophotometer, respectively.

NMR spectra were measured on a Hitachi R-20B spectrometer, using tetramethylsilane as the internal standard.

Mass spectra were obtained with a Hitachi M-52 spectrometer.

1,2-Bis(2-hydroxyethyl-3-phenyl-1-isoindolyl)ethylene [2b]



To a solution of 560 mg of [1] in 12 ml methanol were added 0.3 ml of 2-aminoethanol and 1 ml of acetic acid, and the mixture was allowed to stand at room temperature. After 24 hr, the precipitate was collected and washed with methanol, giving 170 mg of [2b] as red needles; mp 188–189°C. IR(cm^{-1}): 950 (*trans* CH=CH) and 1050 (C–O). MS(m/e): 498(M^+) (base peak).

Found: C, 80.98; H, 6.19; N, 5.44; O, 7.03%. Calcd for $C_{34}H_{30}N_2O_2 \cdot 1/3H_2O$: C, 80.93; H, 6.13; N, 5.55; O, 7.39%.

1,2-Bis(2-methoxyethyl-3-phenyl-1-isoindolyl)ethylene [2c]

By the above described procedure using 2-methoxyethylamine in the place of 2-aminoethanol 180 mg of [2c] was obtained as red crystals; mp 161–163°C.

IR(cm^{-1}): 960 (*trans* CH=CH) and 1115 (C–O–C). MS(m/e): 526(M^+) (base peak).

1,1'-Dihydroxyethyl-5,5'-diphenyl-3,4:3',4'-dibenzo-2,2'-dipyrrromethenium chloride [3b]

To a solution of 560 mg of [1] in 20 ml methanol were added 0.4 ml of 2-aminoethanol and 1 ml of acetic acid, and the mixture was allowed to stand at room temperature. After 24 hr the resulting red precipitate was dissolved on addition of 3 ml of hydrochloric acid. After 3 days, the mixture was evaporated *in vacuo*, and then the residue was extracted with chloroform. After removal of the solvent, the residue was chromatographed on silica gel (Mallinckrodt 100 mesh) using benzene, benzene-ether (9:1), and then acetone-methanol (95:5) as eluent. The third fraction was collected and brought to dryness. The crude product was chromatographed on silica gel using benzene-chloroform-methanol (50:47:3) to give 8 mg of [3b]; mp 203.5–205.5°C (from acetone-methanol). IR(cm^{-1}): 815 (CH=C), 1055 (C–O) and 1603 (conjugated C=N). $\lambda_{\text{Max}}^{\text{MeOH}}$ (nm): 608 ($\epsilon = 71800$); 356 ($\epsilon = 9120$); 297 ($\epsilon = 11600$); 271 ($\epsilon = 16000$), $\lambda_{\text{Max}}^{\text{MeOH}+\text{AcOH}}$ (nm): 608; 356; 297; 271. MS(m/e): 484 ($C_{33}H_{29}N_2O_2 - 1$) (11%); 466 (484 – H_2O) (40%); 446 (484 – $2H_2O - 2H$) (base peak).

Found: C, 75.21; H, 5.77; N, 5.29; O, 7.04; Cl, 6.90%. Calcd for $C_{33}H_{29}N_2O_2Cl \cdot 1/4H_2O$: C, 75.41; H, 5.66; N, 5.33; O, 6.85; Cl, 6.75%.

From the second fraction 33 mg of [4b] was

obtained; mp 197–198.8°C.

1,1'-Dimethoxyethyl-5,5'-diphenyl-3,4:3',4'-dibenzo-2,2'-dipyrrromethenium Chloride [3c]

To the filtrate obtained from the reaction mixture on the preparation of [2c] was added 3 ml of hydrochloric acid, and then the mixture was concentrated *in vacuo*. The residue was treated as above for the isolation of [3b]. From the acetone-methanol fraction 45 mg of [3c] was obtained; mp 140.8–142.0°C (from acetone-ethylacetate).

IR(cm^{-1}): 805 (CH=C), 1140 (C–O–C) and 1600 (conjugated C=N). $\lambda_{\text{Max}}^{\text{MeOH}}$ (nm): 609 ($\epsilon = 81600$); 355 ($\epsilon = 6090$); 297 ($\epsilon = 10800$); 271 ($\epsilon = 15500$), $\lambda_{\text{Max}}^{\text{MeOH}+\text{AcOH}}$ (nm): 609; 355; 296; 270. NMR(δ) ($CDCl_3$): 2.2–2.5 (m, 2H, H_2O); 3.01 (s, 6H, OCH_3); 3.65–4.0 (m, 4H, CH_2-OCH_3); 4.7–5.3 & 5.7–6.3 (b, 4H, $\equiv N^{\delta+}-CH_2$); 7.0–7.9 (m, 18H, aromatic H) 9.53 (1H, conjugated=CH). MS (m/e): 514 ($C_{35}H_{33}N_2O_2 + 1$) (base peak); 454 (513 – C_3H_7O) (86%).

Found: C, 73.85; H, 6.34; N, 4.93; O, 8.33; Cl, 6.55%. Calcd for $C_{35}H_{33}N_2O_2Cl \cdot 1H_2O$: C, 74.12; H, 6.22; N, 4.94; O, 8.46; Cl, 6.25%.

1-Hydroxyethyl-5,5'-diphenyl-3,4:3',4'-dibenzo-2,2'-dipyrrromethene [5b]

To a solution of 224 mg of [1] and 446 mg of 1-hydroxy-3-methyl-1-phenyl-1H-isoindole in 40 ml methanol were added 0.24 ml of 2-aminoethanol and 1 ml of acetic acid, and the reaction mixture was allowed to stand at room temperature. After 24 hr the dark blue precipitate was filtered and washed with methanol, giving 150 mg of [5a]; mp 247–249°C. The filtrate was evaporated *in vacuo*, and the residue was extracted with chloroform. The chloroform layer was concentrated *in vacuo*, and then the residue was chromatographed on silica gel with benzene, benzene-chloroform (1:1) and chloroform-methanol (99:1) as eluent. From the third fraction 10 mg of [5b] was obtained as crystals with metallic luster; mp 180–182°C. IR(cm^{-1}): 822 (CH=C), 1058 (C–O) and 1605 (conjugated C=N). $\lambda_{\text{Max}}^{\text{anhydrous benzene}}$ (nm): 553; 301; 615 (sh), $\lambda_{\text{Max}}^{\text{benzene}+\text{AcOH}}$ (nm): 617 ($\epsilon = 94300$); 395; 299. NMR(δ) ($CDCl_3$): 3.92–4.5 (3H, NCH_2CH_2OH); 4.5–4.85 (2H, CH_2OH); 7.1–8.4 (18H, aromatic H); 9.70 (s, 1H, conjugated=CH). MS(m/e): 440(M^+) (19%); 422($M^+ - H_2O$) (8%); 396($M^+ - C_2H_4O$) (base peak).

Found : C, 77.92 ; H, 5.58 ; N, 5.67%. Calcd for $C_{31}H_{24}N_2O_2H_2O$: C, 78.13 ; H, 5.29 ; N, 5.88%.

1-(3-Phenyl-1-sioindolylidene)methyl-4-phenylphthalazine hydrochloride [6]

A mixture of hydrazine-hydrochloride(1.1 g in 5 ml water) and acetic acid(3 ml) was added to a solution of 1.12 g of [1] in 20 ml ethanol, and the mixture was heated under reflux for 1 hr and then allowed to stand at room temperature. After 3 days, the precipitate was filtered and washed with water, giving 10 mg of [6] as greenish deep blue needles ; mp 179.5–180.7°C. IR(cm^{-1}) : 815(CH=C) ; 1618(conjugated C=N). λ_{max}^{EtOH} (nm) : 622($\epsilon=92800$) ; 576($\epsilon=42100$) ; 326 ; 298($\epsilon=22600$) ; 268($\epsilon=20400$), $\lambda_{max}^{EtOH+AcOH}$ (nm) : 622 ; 326 ; 299 ; 270. MS(m/e) : 410(M^+-Cl) ; 396($410-N_2$)(base peak).

Found : C, 75.03 ; H, 4.97 ; N, 8.97 ; Cl, 7.68%. Calcd for $C_{29}H_{20}N_3Cl.H_2O$: C, 75.07 ; H, 4.78 ; N, 9.06 ; Cl, 7.64%.

1-Methyl-4-phenylphthalazine [7]

The filtrate obtained from the reaction mixture in the preparation of [6] was concentrated *in vacuo*, and the residue was shaken with chloroform and water. The aqueous layer was alkalinized with sodium hydrogencarbonate solution to give 430 mg of [7] as light brown columns ; mp 124.5–125.8°C (from benzene–hexane). The chloroform layer was evaporated and the residue was chromatographed on silica gel using benzene and benzene-ether(4 : 1). From the second fraction also 220 mg of [7] obtained. The structure of [7] was determined by comparison with that of the authentic sample synthesized from 1-phenylphthalazine⁹.

IR(cm^{-1}) : 1610(conjugated C=N). MS(m/e) : 220(M^+)(95%) ; 219(M^+-1)(base peak) ; 192(M^+-N_2)(13%).

The first fraction was concentrated to give 55 mg of [5a] ; mp 248–249.5°C.

Detection of ammonia

A aqueous solution of hydrazine-hydrochloride (1.0g in 5 ml) was kept at 20.0°C and subjected to the detection of liberated ammonia. A certain amount of the solution was made alkaline with aqueous potassium hydroxide solution, and analyzed by gas chro-

matography. The values were calibrated with ammonia solutions of known concentrations.

	24 hr	2 d	5 d	7 d
$NH_3/N_2H_4 \cdot 2HCl (\times 10^{-2} mol)$	0.6	1.1	1.3	1.2

GLC analyses were carried out on a Hitachi 063 Gas Chromatograph with Amipack 124(Gasukuro Kogyo Ltd.).

4-Phenyl-1-phthalazinecarbaldehyde [9]

To a solution of 0.64 g of selenium dioxide in dioxane–water(5.8 ml–0.2 ml) was added dropwise a solution of 1.1 g of [7] in 6 ml dioxane at 45°C with stirring. The mixture was brought to 90°C over a period of 30 min, and refluxed for 30 min. The resulting selenium was filtered off and the filtrate was evaporated *in vacuo*. The residue was chromatographed on silica gel using benzene and benzene–chloroform(1 : 1). From the second fraction 0.64g of [9] was obtained ; mp 147–149°C.

IR(cm^{-1}) : 1710(C=O) ; 2840(aldehyde CH).

λ_{max}^{MeOH} (nm) : 279($\epsilon=8860$) ; 222($\epsilon=44500$).

Found : C, 77.10 ; H, 4.09 ; N, 11.79%. Calcd for $C_{15}H_{10}N_2O$: C, 76.91 ; H, 4.30 ; N, 11.96%.

1,2-Bis(4-phenyl-1-phthalazinyl)ethylene [8]

To a solution of 550 mg of [7] and 590 mg of [9] in 10 ml dimethylformamide was added 170 mg of zinc chloride, the mixture was brought to 100°C over a period of 45 min. The mixture was stirred for 2 hr at 100°C, allowed to cool room temperature, and then the precipitate was filtered and washed with benzene, giving 790 mg(72%) of [8] as yellowish orange needles ; mp 281–283°C.

IR(cm^{-1}) : 965(trans CH=CH). $\lambda_{max}^{chloroform}$ (nm) : 353 ($\epsilon=18700$) ; λ_{max}^{MeOH} (nm) : 345 ; 283. MS(m/e) : 436(M^+)(9%) ; 408(M^+-N_2)(base peak).

Found : C, 81.47 ; H, 4.88 ; N, 12.68%. Calcd for $C_{30}H_{20}N_4 \cdot 1/4H_2O$: C, 81.71 ; H, 4.69 ; N, 12.71%.

References

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