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Color Reaction between Imidazoline and 3,5-Dinitrobenzoyl Chloride, and Determination of Naphazoline in Pharmaceuticals

Tsunetoshi Kaito and Koji Kasuya

Research Laboratory, Taisho Pharmaceutical Co., Ltd.[1]

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Imidazoline was benzoylated with 3,5-dinitrobenzoyl chloride and sodium carbonate buffer by the usual Schotten–Baumann reaction to develop a deep red color. The reaction was carried out in the dark and the solution after addition of 3,5-dinitrobenzoyl chloride to imidazoline was immediately brought to a slightly acidic or neutral pH by which the color developed. This coloration was applied for the determination of naphazoline in pharmaceuticals and the mechanism of this reaction was also investigated.

Many attempts have been made for nucleophilic substitution by a variety of polynitrobenzenes since first noted by Janovsky and Erb.[2] The present paper deals with a kind of Janovsky-type reaction between imidazoline and 3,5-dinitrobenzoyl chloride ($(NO_2)_2BzCl$), involving its analytical application. A solution of $(NO_2)_2BzCl$ in acetone was added to imidazoline in mild sodium carbonate buffer at room temperature and a deep red color developed which had two maxima at 433 and 565 nm, and a best coloration was obtained when the reaction mixture was about pH 5. Under these conditions, no color was produced in the reagent blank. Several methods for the determination of imidazolines are generally based on spectrophotometry by measurement of their ultraviolet (UV) absorptions[3] or by the use of reagents such as sodium nitroprusside,[4] iodine[5] and Bromophenol Blue.[6] Many of these methods are suitable for the determination of naphazoline. The present method is highly specific and can be used directly for the analysis of naphazoline in usual pharmaceutical preparations if there is more than 30 μg of naphazoline per ml of a mixtures.

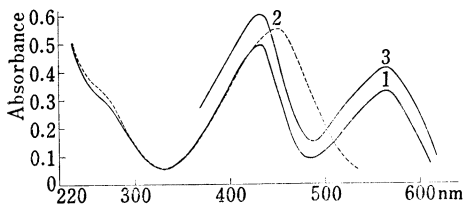


Fig. 1. Absorption Spectra of IIIa (1), IVa (2), and Standard Colored Solution (3) obtained from Naphazoline

final concentration: IIIa and IVa: each 10 μg/ml in 0.95% (v/v) MeOH
Standard colored solution de veloped by analytical procedure: 14.3 μg/ml

Absorption Spectra and Colored Products

Fig. 1 shows the absorption spectra of naphazoline reacted with $(NO_2)_2BzCl$. The visible spectra with two maxima resembled closely that of Meisenheimer-like compounds and when the deep red solution of naphazoline was irradiated by light or exposed to sunlight, the initial two maxima disappeared gradually and a new single maximum appeared at 450 nm. Analogous reactions were observed in related imidazolines and symmetrical disubstituted amidine as illustrated in Chart 1. Tetrahydrozoline, lysidine, acetamidine, and benzylamidine did not show intense color in this reaction. Although the compounds tested were limited, it was found that the formation of a deep red color with $(NO_2)_2BzCl$

1) Location: *3-34-1, Takada, Toshima-ku, Tokyo.*
2) J.V. Janovsky and L. Erb, *Ber.*, **19**, 2115 (1886).
3) *a*) M. Schwartz, R. Kuramoto, and L. Malspeis, *J, Am. Pharm. Assoc.*, **45**, 814 (1956); *b*) M.J. Stern, *Drug Standards*, **26**, 158 (1958).
4) S.C. Slack and M.J. Mader, *J. Am. Pharm. Assoc.*, **46**, 742 (1957).
5) S. Kaga and K. Ōya, *Yakuzaigaku*, **26**, 11 (1969).
6) L.N. Mattson and R.N. Gaeveler, *Drug Standards*, **28**, 77 (1960).

depends on the presence of a methylene group of benzyl or naphthylmethyl type and a secondary amino group, such as the grouping (-N=)-NH-C-CH_2-$C_{10}H_7$, in the molecule. Absorption maxima and molar absorption coefficients of imidazolines and amidine obtained by the present reaction are given in Table I.

In an attempt to clarify the structure of the colored products, acetone was eliminated from the deep red solution (naphazoline, *p*-chlorobenzylimidazoline) by extracting with petroleum ether and benzene. The remaining aqueous solution was slighly acidified with acetic

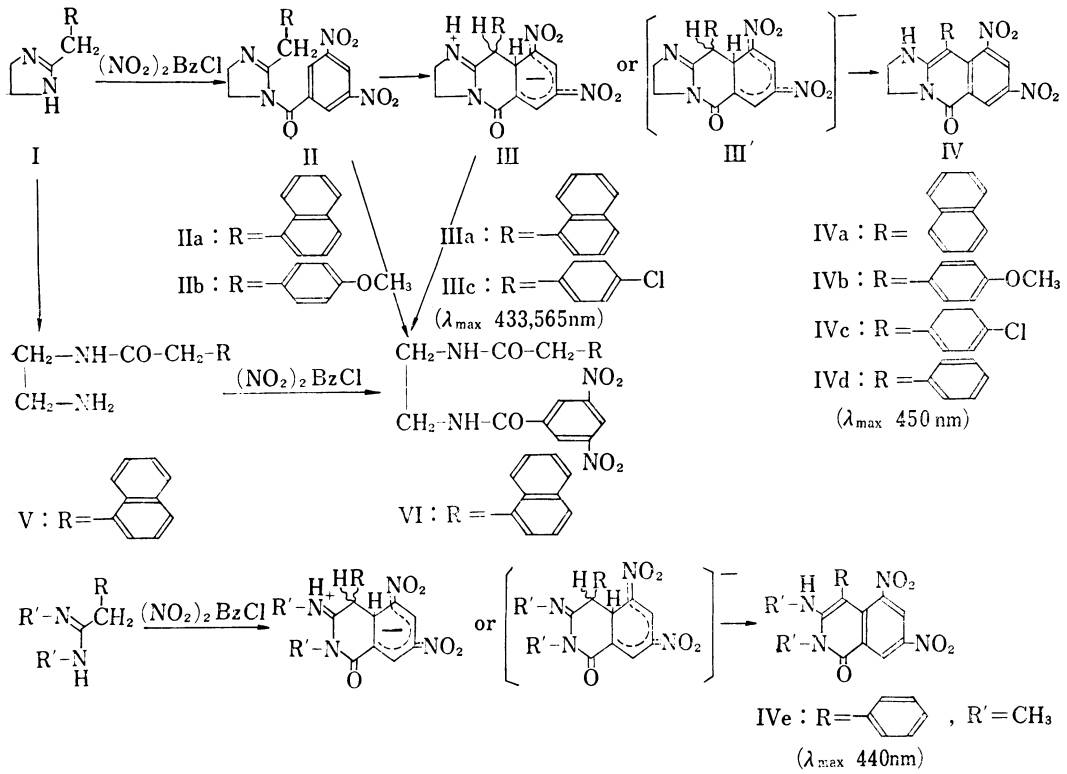


Chart 1. Mechanism of Color Reaction

TABLE I. Absorption Spectra Data of III and IV

	nm[a]	ε A	λmax (nm)	ε A	ε B	λmax (nm)	ε A	ε B
IIIa	270	(11700)	433	(19500)	(21700)	565	(13000)	(14800)
IIIb			433		(10700)	565		(6900)
IIIc	270	(11100)	433	(18500)	(20900)	565	(12100)	(13800)
IIId			433		(13100)	565		(8500)
IIIe			433		(9700)	565		(6100)
IVa	270	(13000)	450	(21900)	(24300)			
IVb	270	(12400)	450	(19200)	(21500)			
IVc	270	(12500)	450	(20600)	(23000)			
IVd	270	(10900)	450	(20000)	(22400)			
IVe	270	(10200)	450	(18800)	(20600)			

IIIb, IIId, and IIIe: Apparent molar absorption coefficients
a) shoulder
A: (solvent): 95% (v/v) MeOH B (solvent): acetone-H_2O (5: 2, v/v)

acid or hydrochloric acid to precipitate a violet compound (IIIa, IIIc), which formed plate crystals and exhibited two intense maxima (433, 565 nm) in the visible region. These spectra were in good agreement with those obtained from naphazoline and *p*-chlorobenzylimidazoline by the standard procedure. On the other hand, when a large amount of imidazoline (naphazoline, *p*-methoxybenzylimidazoline) was used in the color reaction, a compound of yellowish cream color (IIa, IIb) precipitated immediately after the addition of $(NO_2)_2BzCl$, which was obtained as plate crystals. Although the measurement of nuclear magnetic resonance (NMR) spectrum of IIa was impossible due to its limited solubility, the NMR spectrum of IIb indicated the presence of 5-substituted 1,3-dinitrobenzene ring at 8.80 δ (1H, triplet) and 8.63 δ (2H, doublet), *p*-methoxyphenyl group at 6.70—7.12 δ (4H, quartet), and 3.78 δ (3H, singlet), two methylene groups of imidazoline at 3.87 δ (4H, singlet), and methylene protons of benzyl group at 3.70 δ (2H, singlet). These compounds were assigned to 1-(3,5-dinitrobenzoyl)imidazolines (II) by further reference to their infrared (IR) spectra and elemental analytical data. However, when the IIa was dissolved in dimethylformamide (DMF), the solution altered gradually to a deep red solution in the absence of alkali. When allowed to stand in a refrigerator, the deep red solution began to crystallize as violet plates, which was identified with IIIa by the comparison of IR and visible absorption spectra. As described above, the violet compound (IIIa) was obtained by addition of a small amount of acid to naphazoline chromophore, but when the amount of acid was increased, the naphazoline chromophore changed to a colorless solution and the solution finally gave a white precipitate, which was proved to be identical with the authentic sample of 1-naphthylacetyl-1′-(3,5-dinitrobenzoyl)ethylenediamine[7] (VI) by a mixed melting point measurement and comparison of their IR spectra. There might be a path to VI through IIa from IIIa, but IIa could not be isolated from IIIa. A reddish orange compound (IV) was obtained from the colored solution of the

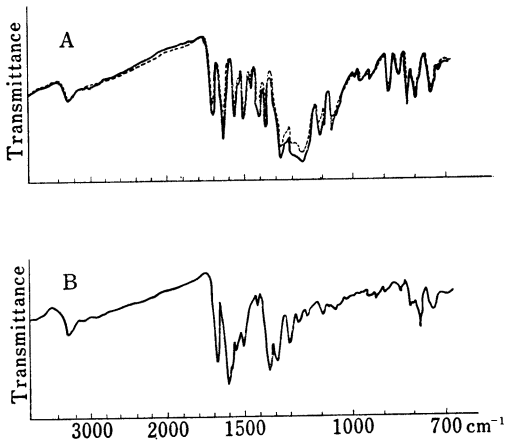


Fig. 2. IR Spectra (KBr) of IIIa (A) and IVa (B) obtained from Naphazoline

IIIa (------) was obtained from IIa.

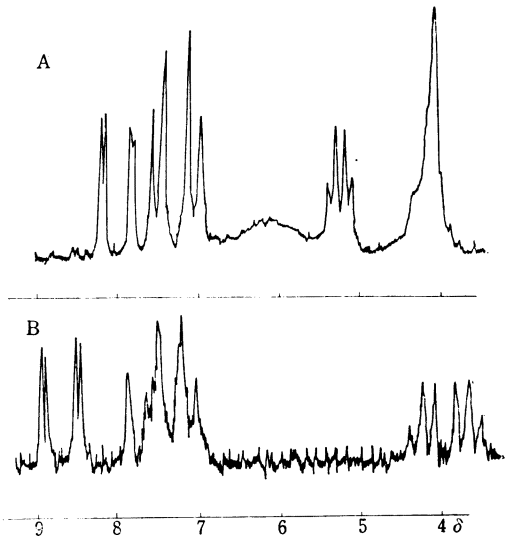


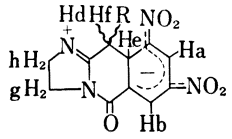
Fig. 3. NMR Spectra of IIIc (A) and IVc (B) obtained from *p*-Chlorobenzylimidazoline

corresponding III by irradiation of light. After evaporation of the irradiated solution, the residue was chromatographed on acidic alumina, and plate or needle crystals were obtained.

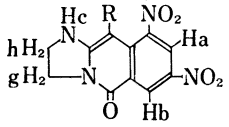
7) VI was prepared by the treatment of one equivalent of 1-naphthylacetylethylenediamine (V) with one equivalent of $(NO_2)_2BzCl$ in the presence of alkali (*cf.* S.R. Aspinall, *J. Am. Chem. Soc.*, **63**, 852 (1941)). V was prepared from naphazoline by a known method.[3a]

The visible spectra of IV showed a single maxima at 450 nm for imidazolines and at 440 nm. for amidine. The IR spectra of the colored products of naphazoline (IIIa, IVa) are given in Fig. 2. The IR absorption of IIIa is similar to that of a typical Meisenheimer compounds in which a series of a strongly overlapping bands between 1310 and 1110 cm^{-1} as noted by Dyall[8] is observed. The NH absorption in both IIIa and IVa appears at the same 3260 cm^{-1} and in the case of IIIa, it was assumed as N^+H absorption. The NMR spectra of III and IV are shown in Fig. 3 and in Table II. In the NMR spectra of IIIc, two coupled absorptions perhaps

TABLE II. NMR Data (δ) of III and IV in Deuterated Dimethyl Sulfoxide



III



IV

	Ha	Hb	Hc	Hd	He	Hf	Hg	Hh
IIIa	*a*)	*a*)	—	*b*)	5.83 (d)	5.39 (d)	4.12 (m)*c*)	
IIIc	8.15 (d)	7.80 (d)	—	6.00 (br.s)*d*)	5.29 (d)	5.11 (d)	4.07 (m)*c*)	
IVb	8.82 (d)	8.36 (d)	7.65 (s)	—	—	—	4.24 (t)	3.78 (t)
IVc	8.84 (d)	8.46 (d)	7.82 (s)	—	—	—	4.24 (t)	3.74 (t)
IVd	8.85 (d)	8.44 (d)	7.72 (s)	—	—	—	4.27 (t)	3.66 (t)
IVe*e*)	8.93 (d)	8.35 (d)	6.27 (br.s)	—	—	—	3.56 (s)	3.09 (s)

The abbreviations s, br. s, d, t, and m denote singlet, broard singlet, doublet, triplet, and multiplet, respectively
J_{ab} *ca.* 2.0 cps (all III and IV), J_{gh} *ca.* 9.0 cps (all IV), J_{ef} 4.9 cps (IIIa), 4.6 cps (IIIc).
a) covered by the R (naphthyl ring) protons
b) Could not ascertained the signal of the N^+H proton
c) The signals of Hg and Hh protons overlapped with each other.
d) Disappeared by adding D_2O or by standing
e) amidine derivative

due to He and Hf as doublets (J=4.6 cps) were observed. It seemed probable from this observation that the methylene group at the 2-position of imidazoline was condensed with the SP^2 hybridized carbon atom in *m*-dinitrobenzene ring to yield a Janovsky compound. As seen in Fig. 3(A), the broad peak at about 6.0 δ would be an N^+H proton of IIIc. Upon standing, however, the broad peak disappeared within about 15 min. It was not obvious whether the N^+H proton of IIIa in its NMR spectrum would exist or not. On the contrary, the reddish orange compound (IV) was much more stable, in which the coupled absorptions of two protons (He, Hf) present in III disappeared. These results suggested that, in the color reaction with $(NO_2)_2BzCl$, an intermolecular cyclization took place after benzoylation of imidazoline. The structure of the violet compound was assumed as III shown in Chart 1 from various analytical results, but its structure might be a type of III' because of using acid during its isolation. The reddish compound also appeared to be compatible with the structure of IV as shown in Chart 1. The elemental analyses of the colored products are summarized in Table III.

Analytical Conditions for the Reaction

Relation between the concentration of sodium carbonate buffer and that of $(NO_2)BzCl$ for this reaction was the most important factor. When the concentration of $(NO_2)_2BzCl$ was varied, while other conditions were held constant in accordance with analytical procecure, the naphazoline curves shown in Fig. 4 were obtained. The concentration of $(NO_2)_2BzCl$ required

8) L.K. Dyall, *J. Chem. Soc.*, **1960**, 5160.

Table III. Elemental Analyses and Melting Points of III and IV

Compounds	mp (°C) (decomp.)	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N
IIIa	257—260[a)]	$C_{21}H_{16}O_5N_4$	62.37	3.99	13.86	62.22	4.09	13.82
IIIc	137—140[a)]	$C_{17}H_{13}O_5N_4Cl$	52.52	3.37	14.41	52.50	3.45	14.40
IVa	320—323	$C_{21}H_{14}O_5N_4$	62.68	3.51	13.92	62.57	3.57	14.01
IVb	271—273	$C_{18}H_{14}O_6N_4$	56.55	3.69	14.65	56.49	3.71	14.70
IVc	292—293	$C_{17}H_{11}O_5N_4Cl$	52.80	2.87	14.49	52.84	2.86	14.50
IVd	285—286	$C_{17}H_{12}O_5N_4$	57.96	3.43	15.90	58.16	3.47	16.01
IVe	244—246	$C_{17}H_{14}O_5N_4$	57.63	3.98	15.81	57.72	3.93	15.90

a) IIIa and IIIc (violet compounds) turned reddish orange at the temperatures of the melting point and decomposed at near the temperature of the melting point of IVa and IVc, respectively.

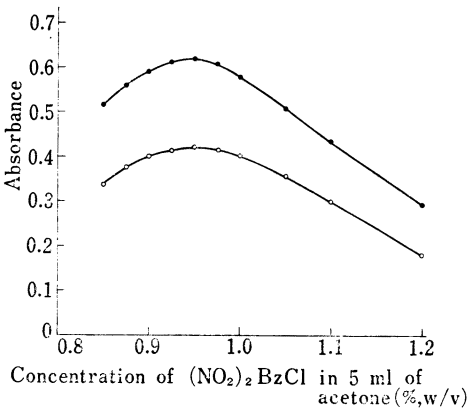


Fig. 4. Effect of Concentration of $(NO_2)_2$-BzCl on Color Intensity

—●—: at 433 nm, —○—: at 565 nm
final concentration of naphazoline: 14.3 μg/ml

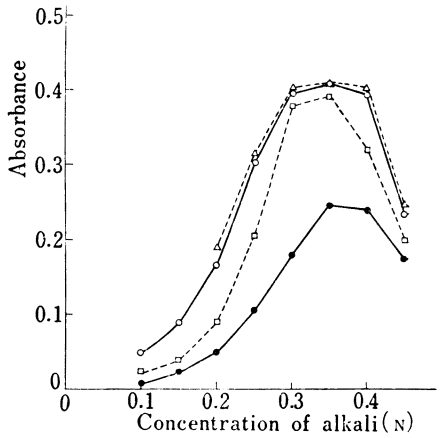


Fig. 5. Effect of Concentration of Alkalis on Color Intensity at 565 nm

—○—: Na_2CO_3, —●—: $NaHCO_3$,
---□---: $Na_2B_4O_7$, ---△---: Na_2CO_3 containing 0.25 ml/ml of phosphate buffer (pH 7.2)
final concentration of naphazoline: 14.3 μg/ml

for the optimum sensitivity was 0.95% (w/v) for naphazoline and 0.90% (w/v) for other imidazolines although the latter is not shown here. The effect of concentration of alkali solutions on color intensity of naphazoline is given in Fig. 5. The maximum absorbance at 565 nm was obtained by using approximately 0.35 N alkalis. Among them, sodium carbonate of 0.35 N was selected and employed as a mixture which contained phosphate buffer (pH 7.2), 0.25 ml per ml, and many preparations containing naphazoline could be successfully analyzed by using this solution. The rate of formation of color between naphazoline and benzyl-type imidazoline with $(NO_2)_2$BzCl differed and increased with time, up to a maximum absorbance at about 2 hr for the former and at about 30 min for the latter, as shown in Fig. 6. The color intensity was stable within about 3 hr after reaching each maximum absorbance at room temperature in the dark. A linear relationship was obtained at 565 nm in the range of 20—200 μg of the imidazolines in the final solution (Fig. 7).

Although the measurement of absorbance at 433 nm was suitable, some compounds which underwent benzoylation by this procedure produced a yellow color and therefore the

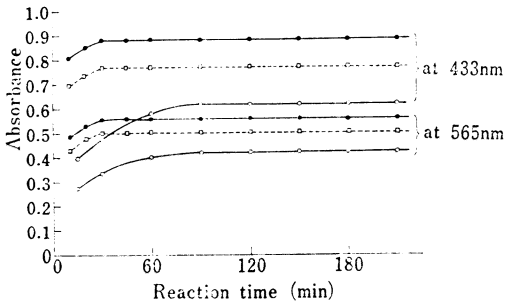


Fig. 6. Rate of Color Development with Naphazoline (—○—) Using 0.95 % (w/v) of Acetone Solution of $(NO_2)_2BzCl$ and with Tolazoline (—●—) and *p*-Chlorobenzylimidazoline (---□---) Using 0.90 % (w/v) Acetone Solution of $(NO_2)_2BzCl$

final concentrations: 14.3 μg/ml

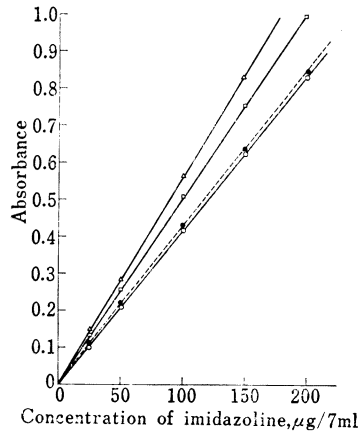


Fig. 7. Calibration Curves for Naphazoline (—○—), *p*-Methoxybenzylimidazoline (—●—), Tolazoline (—△—), and *p*-Chlorobenzylimidazoline (—□—) at 565 nm

Table IV. Recovery of Naphazoline in Some Formulations determined by the Standard Procedure

Naphazoline formulation	Nominal (mg/100 ml)	Found[a] (mg/100 ml)	Standard deviation (%)
Ophthalmic	5	5.01	±1.2
Ophthalmic	3	3.02	±1.0
Rhinologic	50	50.02	±1.0
Rhinologic	50	50.03	±1.1

a) mean value of at least five determinations

wavelength at 565 nm was mainly taken for the determination of naphazoline in pharmaceutical preparations. The use of acetone as a solvent for $(NO_2)_2BzCl$ in the reaction gave reproducible results. Table IV shows the analyses of formulated naphazoline.

Experimental[9]

Reagents——(1) $(NO_2)_2BzCl$: Merck reagent (GR) was used and suitable for analysis. Solutions of 0.90 and 0.95% (w/v) $(NO_2)_2BzCl$ in acetone were prepared just before use.[10] (2) Na_2CO_3 buffer: A mixture of 1.855 g of Na_2CO_3, 165.6 mg of Na_2HPO_4, and 68.0 mg of KH_2PO_4 was dissolved in about 50 ml of H_2O and the solution was diluted to 100 ml with H_2O. This solution was equivalent to 0.35N Na_2CO_3 which further contained 0.25 ml of Sörensen's phosphate buffer (pH 7.2) in ml. (3) Imidazoline and amidine derivatives were obtained from commercial sources or synthesized by known or obvious procedures,[11,12] and used as their hydrochlorides.

9) All melting points are uncorrected. The UV and visible spectra were recorded on a Hitachi EPS-2U. The IR spectra were measured on a Nihon Bunko DS-301 and the NMR spectra on a Hitachi Perkin-Elmer R-20 at 60 Mc using tetramethylsilane as an internal standard.

10) A solution of 0.90% (w/v) $(NO_2)_2BzCl$ in acetone was used for compounds other than naphazoline unless otherwise stated.

11) A. Sonn, U.S. Pat. 2161938 (1939) [J.P. VII, c-313].

12) G. Luckenbach, *Ber.*, **17**, 1421 (1884).

Analytical Procedure for Naphazoline——To 1 ml of the test solution containing about 100 μg/ml of naphazoline, 1 ml of 0.35N Na_2CO_3 buffer and 5 ml of 0.95% (w/v) $(NO_2)_2BzCl$ in acetone were added and mixed. The solution was allowed to stand for 2 hr at room temperature in the dark and the absorbance was measured against a reagent blank at 565 nm (or 433 nm).

1-(3,5-Dinitrobenzoyl)imidazoline (IIa, IIb)——IIa: To a solution of 1 g of naphazoline in 50 ml of H_2O, 50 ml of 0.35N Na_2CO_3 buffer and 250 ml of 0.95% (w/v) $(NO_2)_2BzCl$ in acetone were added and mixed. The resulting precipitate was collected immediately by filtration and washed with a small quantity of acetone. Recrystallization from DMF–MeOH (1: 3) gave IIa as yellowish cream colored plates, mp 153—156°. Yield, 400 mg. *Anal.* Calcd. for $C_{21}H_{16}O_5N_4$: C, 62.37; H, 3.99; N, 13.85. Found: C, 62.25; H, 3.98; N, 13.80. IR ν_{max}^{KBr} cm^{-1}: 1675 (CO), 1650 (CN), 1540, 1350 (NO_2).

IIb: To a solution of 1.5 g of *p*-methoxybenzylimidazoline in 50 ml of H_2O, 50 ml of 0.35N Na_2CO_3 buffer and 250 ml of 0.90% (w/v) $(NO_2)_2BzCl$ in acetone were added, mixed, and treated in the same manner as described above. Recrystallization from acetone–ether (1: 3) gave IIb as yellowish cream colored plates, mp 133—136°. Yield, 500 mg. *Anal.* Calcd. for $C_{18}H_{16}O_6N_4$: C, 56.25; H, 4.26; N, 14.58. Found: C, 56.28; H, 4.22; N, 14.67. IR ν_{max}^{KBr} cm^{-1}: 1668 (CO), 1633 (CN), 1546, 1368 (NO_2). NMR spectral data are given in the earlier page.

Preparation of Colored Products (IIIa, IIIc)——IIIa: To a solution of 150 mg of naphazoline in 50 ml of H_2O, 50 ml of 0.35N Na_2CO_3 buffer and 250 ml of 0.95% (w/v) $(NO_2)_2BzCl$ in acetone were added and mixed. The reaction mixture was allowed to stand for 2 hr at room temperature in the dark and acetone was extracted from the colored solution first with petr. ether and next with petr. ether–benzene by gradually increasing the amount of benzene, and the extract was discarded. Five ml of AcOH or 0.1N HCl was added to the remaining aqueous solution to precipitate a violet compound, which was collected by filtration and washed with EtOH–ether (1: 2). Recrystallization from DMF–MeOH (1: 4) gave IIIa as violet plates (in this case, IIIa was first dissolved in DMF, to which was added MeOH). Yield, 50 mg. IR ν_{max}^{KBr} cm^{-1}: 3260 (N^+H), 1690 (CO), 1625 (CN), 1546, 1337 (NO_2).

IIIc: A solution of 500 mg of *p*-chlorobenzylimidazoline in 50 ml of H_2O was treated with 50 ml of 0.35N Na_2CO_3 buffer and 250 ml of 0.90% (w/v) $(NO_2)_2BzCl$ in acetone by the same procedure as above. Recrystallization from DMF–MeOH (1: 4) gave IIIc as violet plates (method of recrystallization the same as that of IIIa). Yield, 100 mg. IR ν_{max}^{KBr} cm^{-1}: 3250 (N^+H), 1705 (CO), 1620 (CN), 1555, 1330 (NO_2).

Other compounds of III could not be isolated in pure states.

Preparation of IIIa from IIa——To 250 ml of DMF was added 500 mg of IIa protected from light and heated at about 40° for 20 min with stirring. The solution was filtered and the filtrate was allowed to stand for 2 hr at room temperature in the dark and then in a refrigerator overnight. The violet crystals that formed were collected, washed with EtOH–ether (1: 2), and dried over P_2O_5 *in vacuo*. Yield, 100 mg. The compound was proved to be identical with IIIa from their IR and visible spectra.

1-Naphthylacetyl-1′-(3,5-dinitrobenzoyl)ethylenediamine (VI)——To a solution of 100 mg (4.4×10^{-4}M) of 1-naphthylacetylethylenediamine (V) in 20 ml of $CHCl_3$, 40 mg (5.0×10^{-4}M) of pyridine and a solution of 102 mg (4.4×10^{-4}M) of $(NO_2)_2BzCl$ in 20 ml of benzene were added and mixed. The solution was allowed to stand for 1 hr at room temperature and then in a refrigerator overnight. The resulting white precipitate was collected and washed with benzene. Recrystallization from EtOH–acetone (1: 1) gave VI as almost colorless needles, mp 214—216°. Yield, 80 mg. IR ν_{max}^{KBr} cm^{-1}: 3275 (NH), 1642 (CO), 1542, 1347 (NO_2).

Decomposition of Colored Products——IIIa→VI: To a solution of 50 mg of IIIa in 30 ml of DMF, 5 ml of 10% H_2SO_4 solution was added. The solution was allowed to stand for 24 hr at room temperature and diluted with 70 ml of H_2O. The resulting white precipitate was collected and washed with EtOH–H_2O (1: 1). Recrystallization from EtOH–acetone (1: 1) gave almost colorless needles, mp 214—216°, which was proved to be identical with VI by a mixed melting point measurement and the comparison of their IR spectra. Yield, 25 mg. *Anal.* Calcd. for $C_{21}H_{18}O_6N_4$: C, 59.91; H, 4.30; N, 13.26. Found: C, 59.85; H, 4.34; N, 13.27.

IIa→VI: A solution of 50 mg of IIa in 30 ml of DMF was treated with 5 ml of 10% H_2SO_4 solution in the same manner as above. Recrystallization from EtOH–acetone (1: 1) gave almost colorless needles, mp 214—216°, which was proved to be identical with VI by a mixed melting point measurement and the comparison of their IR spectra. Yield, 25 mg.

Preparation of Colored Products (IVa—IVe)——IVa: (a) A solution of 100 mg of IIIa in 60 ml of DMF was irradiated from an UV lamp (254 nm) at a distance of about 5 cm for 5—6 hr or exposed to sunlight for 6—8 hr. After evaporation of the solvent *in vacuo*, the residue was purified by column chromatography on 100 g of acidic alumina using acetone–ether (1: 1) as an eluting solvent. The orange colored fraction eluted first with this solvent, which exhibited a single maximum at 450 nm in the visible region, was collected and concentrated. Recrystallization of the eluate from acetone–MeOH (1: 1) gave IVa as reddish orange plates. Yield, 50 mg. IR ν_{max}^{KBr} cm^{-1}: 3260 (NH), 1664 (CO), 1536, 1327 (NO_2).

(b) A colored solution, obtained from 150 mg of naphazoline described in the preparation of colored products (IIIa), was irradiated with UV lamp or exposed to sunlight and then by column chromatography in the same manner as above. Recrystallization from acetone–MeOH (1: 1) gave IVa as reddish orange plates. Yield, 50 mg.

Other colored products (IVb—IVe) were obtained by the same procedures as described above. Yield, 40—50 mg each. IVb: Reddish orange plates. IR ν_{max}^{KBr} cm^{-1}: 3400 (NH), 1670 (CO), 1537, 1325 (NO_2). IVc: Reddish orange plates. IR ν_{max}^{KBr} cm^{-1}: 3230 (NH), 1667 (CO), 1535, 1332 (NO_2). IVd: Reddish orange plates. IR ν_{max}^{KBr} cm^{-1}: 3290 (NH), 1678 (CO), 1533, 1327 (NO_2). IVe: Reddish needles. IR ν_{max}^{KBr} cm^{-1}: 3380 (NH), 1672 (CO), 1560, 1328 (NO_2).

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