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Studies on Aromatic Nitro Compounds. II.[1] Reaction of 2-Nitronaphthalene with Malononitrile in the Presence of Bases

Toshihiko Ohshima, Yukihiko Tomioka, and Motoyoshi Yamazaki*

Faculty of Pharmaceutical Sciences, Fukuoka University, 11 Nanakuma, Nishi-ku, Fukuoka 814-01, Japan

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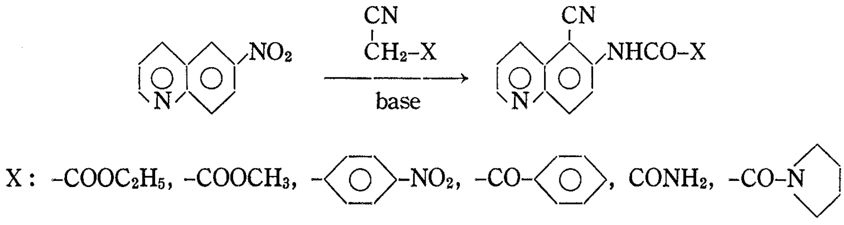
Treatment of 2-nitronaphthalene with malononitrile and potassium hydroxide gave the potassium salt (II) of 1,1-dicyano-2-hydroxy-2-(1-cyano-2-naphthylamino)ethylene (II′) in 78% yield. II was hydrolyzed to 2-aminonaphthalene *via* 3-dicyanomethylene-3,4-dihydro-1H-naphth[2,1-*d*][1,3]oxazin-1-one (III) when heated with 20% hydrochloric acid. III reacted with amines to form benzo[*f*]quinazolines (IVa—d). II was treated with hydrochloric acid in pyridine to yield the pyridinium salt (IIa) of II′, and IIa was converted to II by treatment with potassium acetate. II was also synthesized from ethyl N-(1-cyano-2-naphthyl)carbamate, malononitrile and potassium amide.

Keywords——2-nitronaphthalene; malononitrile; 1,1-dicyano-2-hydroxy-2-(1-cyano-2-naphthylamino)ethylene; hydrolysis; potassium hydroxide; 2-substituted 1,3-dioxo-1,2,3,4-tetrahydrobenzo[*f*]quinazolines; acylation; ethyl N-(1-cyano-2-naphthyl)-carbamate

In a previous paper, we showed that 6-nitroquinoline reacts with some cyanomethylene compounds in the presence of a base to form 6-aminoquinoline-5-carbonitrile derivatives as the main products.[1]



As a sequel to this study, we now describe the reaction of 2-nitronaphthalene (I) with malononitrile in the presence of a base.

When a solution of I, malononitrile and potassium hydroxide in dimethylformamide (DMF) was stirred at room temperature for 24 hr, the potassium salt (II) of 1,1-dicyano-2-hydroxy-2-(1-cyano-2-naphthylamino)ethylene (II′) was obtained. Various conditions for this reaction were examined and the results listed in Table I were obtained.

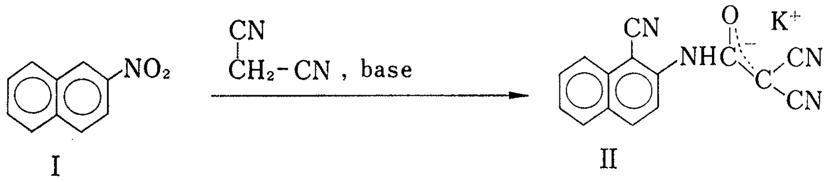
Potassium hydroxide was shown to be the most effective base. The reaction of I with malononitrile (3 equiv.) and potassium hydroxide (3 equiv.) produced II in the best yield (78%). However, when 1.2 equivalents of malononitrile and potassium hydroxide were used, II was obtained in a low yield of 23%. The use of potassium *tert*-butoxide or potassium amide instead of potassium hydroxide also gave II in somewhat lower yields of 41 and 45%, respectively.

The potassium salt (II) was recrystallized from aqueous methanol as colorless feathery crystals, mp 298° (dec.). Its infrared (IR) spectrum showed two nitrile bands at 2185 and 2160 cm^{-1} and an amine band at 3320 cm^{-1}.

Chart 1 illustrates the reactions carried out in connection with the structural elucidation of II.

When II was refluxed with 20% hydrochloric acid for 48 hr, the product proved to be 2-aminonaphthalene rather than the expected 2-aminonaphthalene-1-carbonitrile.[2] However,

TABLE I. Reaction of 2-Nitronaphthalene (I) with Malononitrile in the Presence of a Base



I	Molar ratio $CH_2(CN)_2$	Base	Yield of II (%)
1	1.2	KOH 1.2	23
1	2	KOH 2	40
1	3	KOH 3	78
1	3	*tert*-BuOK 3	41
1	3	KNH_2 4	45

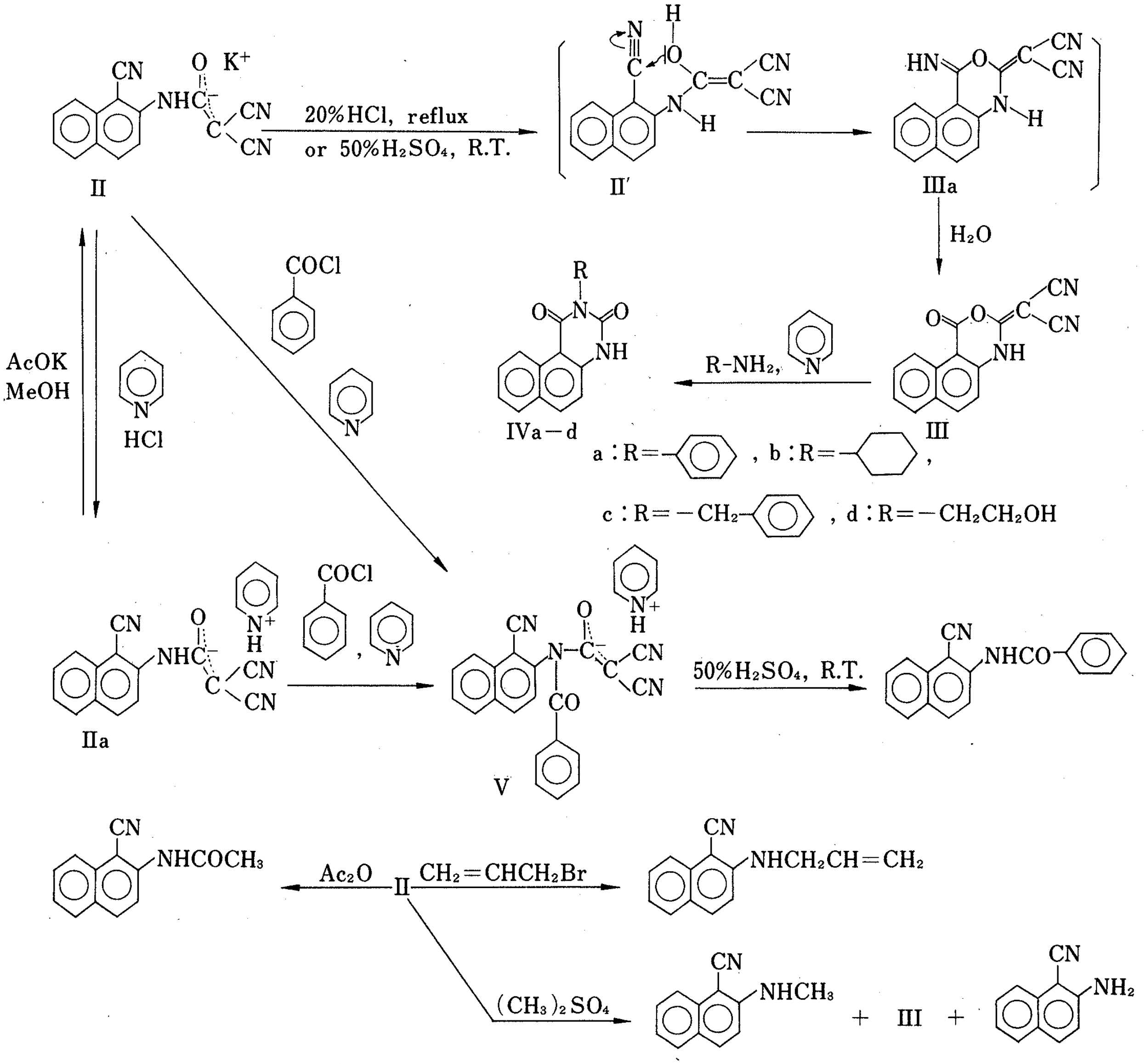


Chart 1

on short boiling (3 hr) in 20% hydrochloric acid, II was converted to 3-dicyanomethylene-3,4-dihydro-1H-naphth[2,1-*d*][1,3]oxazin-1-one (III), which was hydrolyzed to 2-aminonaphthalene on prolonged heating with 20% hydrochloric acid. On the other hand, 2-aminonaphthalene-1-carbonitrile was recovered from boiling 20% hydrochloric acid after 50 hr. These findings indicate that the hydrolysis of II to 2-aminonaphthalene proceeds *via* III rather than 2-aminonaphthalene-1-carbonitrile. The treatment of II with 50% sulfuric acid at room temperature gave also III in 74% yield. All attempts to isolate II′ from II were unsuccessful. III was recrystallized from acetone to form greenish-yellow needles, mp 320° (dec.). The results of elemental analysis and the mass spectrum (M^+: m/e 261) indicated that this compound had the molecular composition $C_{15}H_7N_3O_2$. Its IR spectrum exhibited a characteristic conjugated nitrile band at 2200 cm^{-1} and a strong band at 1775 cm^{-1} indicative of a lactone carbonyl group. The proton magnetic resonance (PMR) spectrum showed a one-proton broad singlet at δ 9.85 due to an amine proton, five aromatic protons (multiplet) at δ 7.47—8.45, and a downfield doublet at δ 9.07 assignable to the proton at C-10. The formation of III can be explained by the scheme shown in Chart 1; II is converted by acidification to II′, which undergoes intramolecular cyclization to form the imino compound (IIIa), and then IIIa is hydrolyzed to III.

In order to confirm the structure of III, the treatment of III with aniline in refluxing pyridine was carried out for 3 hr to give 2-phenyl-1,3-dioxo-1,2,3,4-tetrahydrobenzo[*f*]-quinazoline (IVa) in 83% yield. The reactions of III with cyclohexylamine, benzylamine and ethanolamine under the same conditions gave the corresponding benzo[*f*]quinazolines (IVb, IVc and IVd) in yields of 82, 66 and 53%, respectively. The structural assignments of the benzo[*f*]quinazolines (IV) were made on the basis of elemental analysis (Table II) and the spectral data (Table III).

The IR spectra of IV displayed bands in the 1700—1712 cm^{-1} and 1645—1655 cm^{-1} regions attributable to an imide carbonyl group and in the 3345—3380 cm^{-1} region due to an amino group, but lacked a characteristic nitrile band. Their PMR spectra showed peaks of six aromatic protons of the benzo[*f*]quinazoline moiety including a downfield doublet at δ 9.68—9.86 assigned to the proton at C-10 and the amido proton at δ 11.80—13.0 in addition to the protons of the 2-substituents. Consequently, IV (a—d) were identified as the 2-substituted 1,3-dioxo-1,2,3,4-tetrahydrobenzo[*f*]quinazolines.

On acetylation with acetic anhydride, II gave 2-acetoaminonaphthalene-1-carbonitrile, which was identical with an authentic sample.[2] On the other hand, when II was treated with I equivalent of benzoyl chloride in pyridine, no benzoylation occurred, and the pyridinium salt (IIa) of II′ was obtained in 63% yield. The IR spectrum of IIa exhibited absorption bands at 2400—2880 cm^{-1} due to an ammonium group, and no band due to a carbonyl group

TABLE II. Some Properties of 2-Substituted 1,3-Dioxo-1,2,3,4-tetrahydrobenzo[*f*]quinazolines (IV)

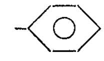
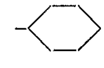
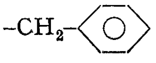
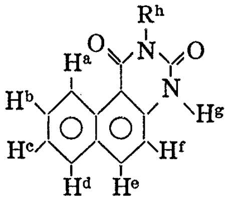
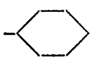
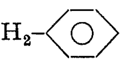
Compd. No.	R	mp (°C) ( ): Recrystn. solvent	Appearance (colorless)	Formula	Analysis (%) Calcd (Found) C	H	N
IVa		343 (dec.)	Needles	$C_{18}H_{12}N_2O_2$	74.99 (75.06	4.20 3.83	9.72 10.15)
IVb		294 (dec.)	Needles	$C_{18}H_{18}N_2O_2$	73.45 (73.11	6.16 6.13	9.52 9.58)
IVc		284 (dec.)	Needles	$C_{19}H_{14}N_2O_2$	75.48 (75.46	4.67 4.35	9.27 9.57)
IVd	$-CH_2CH_2OH$	267 (dec.)	Needles	$C_{14}H_{12}N_2O_3$	65.62 (65.59	4.72 4.54	10.93 11.26)

Table III. Spectral Data for 2-Substituted 1,3-Dioxo-1,2,3,4-tetrahydrobenzo[*f*]quinazolines (IV)



Compd. No.	R	IR ν_{max}^{KBr} cm^{-1}		Proton NMR spectra ppm (J in Hz)								MS m/e (M+)
		NH(OH)	CO	H^a	H^b	H^c	H^d	H^e	H^f	H^g	H^h	
IVa		3360	1712 1654	a)9.72 (d, $J_{a,b}=9$; d, $J_{c,d}=8$; d, $J_{e,f}=9$)	7.28—7.78 (m)	8.24	8.62	7.87	12.92 (br. s)		7.28—7.78 (5H, m)	288
IVb		3350	1705 1654	a)9.78 (d, $J_{a,b}=8.5$; d, $J_{c,d}=8$; d, $J_{e,f}=9$)	7.50—7.78 (m)	8.16	8.54	7.74	12.61 (br. s)		1.18—2.06 (10H, m) 4.98 (1H, m)	294
IVc	$-CH_2-$	3345	1705 1645	a)9.86 (d, $J_{a,b}=9$; d, $J_{c,d}=9$; d, $J_{e,f}=9.5$)	7.38—7.85 (m)	8.33	8.71	7.91	13.10 (br. s)		5.35 (2H, s) 7.38—7.85 (5H, m)	302
IVd	$-CH_2CH_2OH$	3380	1700 1655	b)9.68 (d, $J_{a,b}=9$; d, $J_{c,d}=8$; d, $J_{e,f}=9$)	7.46—7.84 (m)	8.00	8.22	7.38	11.80 (br. s)		3.64 (2H, q, $J=6.5$) 4.12 (2H, t, $J=6.5$) 4.80 (1H, t, $J=6.5$)	256

Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; br.s, broad singlet; m, multiplet.
a) In HMPA-d_{18}. *b*) In DMSO-d_6.

was observed. Its analytical values were consistent with the empirical formula $C_{20}H_{13}N_5O$. II was easily converted to IIa by treatment with hydrochloric acid in pyridine, and conversely, IIa was transformed into II by treatment with potassium acetate in methanol. When II was allowed to react with an excess of benzoyl chloride (2.65 equiv.) in pyridine, the pyridinium salt (V) of 1,1-dicyano-2-hydroxy-2-(N-benzoyl-1-cyano-2-naphthylamino)ethylene was formed in 20% yield together with IIa (30%). The reaction of IIa with 2 equivalents of benzoyl chloride in pyridine also produced V in 40% yield. The product V had the empirical formula $C_{27}H_{17}N_5O_2$, and its IR spectrum showed a carbonyl band at 1670 cm^{-1} and three nitrile bands at 2160, 2180 and 2215 cm^{-1}. V was treated with 50% sulfuric acid at room temperature to produce 2-benzoylaminonaphthalene-1-carbonitrile in 52% yield besides pyridine (identified as its picrate, mp 166°). 2-Benzoylaminonaphthalene-1-carbonitrile was proved to be identical with an authentic sample prepared by benzoylation of 2-aminonaphthalene-1-carbonitrile. V was hydrolyzed on heating with 20% hydrochloric acid for a long period of time to provide 2-aminonaphthalene and benzoic acid in good yields.

The allylation of II with allyl bromide gave 2-allylaminonaphthalene-1-carbonitrile in 45% yield. The reaction of II with dimethyl sulfate resulted in the formation of 2-aminonaphthalene-1-carbonitrile, 2-methylaminonaphthalene-1-carbonitrile and III in yields of 34, 6 and 18%, respectively.

On the basis of these observations, II was assigned as the potassium salt of II'. In order to confirm the structure of II, a method for synthesizing II by an alternative route was investigated (Chart 2). The reaction of 2-aminonaphthalene-1-carbonitrile with ethyl chloroformate in pyridine gave ethyl N-(1-cyano-2-naphthyl)carbamate in 70% yield. When a solution of ethyl N-(1-cyano-2-naphthyl)carbamate and malononitrile in the presence of potassium amide in DMF was heated at 100° for 4 hr, the potassium salt was obtained in 63% yield. Its IR spectrum was identical with that of II.

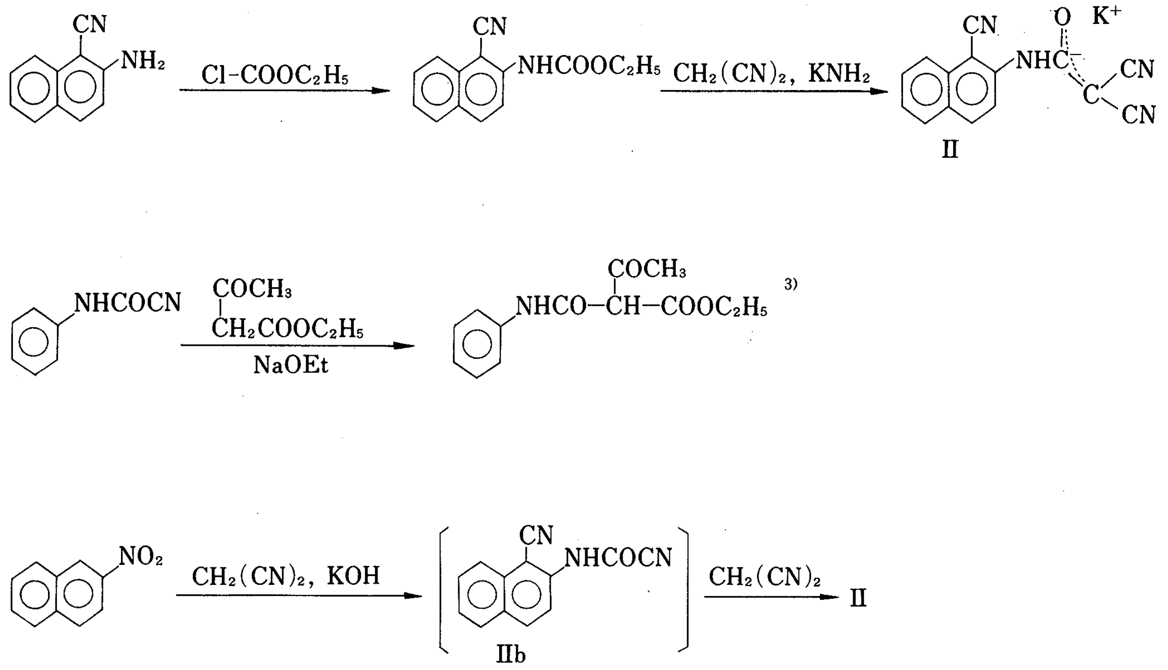


Chart 2

Although the mechanism for the reaction of 2-nitronaphthalene (I) with malononitrile is not clear at present, 6-nitroquinoline reacts with ethyl cyanoacetate under the same conditions to form 6-ethoxalylaminoquinoline-5-carbonitrile,[1] and the reaction of phenylcarbamoyl cyanide with ethyl acetoacetate in the presence of sodium ethoxide yields ethyl phenylcarbamoylacetoacetate.[3] On the basis of the results presented above, it is assumed that the initial reaction of I with malononitrile produces the intermediate 1-cyano-2-naphthylcarbamoyl cyanide (IIb) corresponding to 6-ethoxalylaminoquinoline-5-carbonitrile, and then IIb reacts with another molecule of malononitrile in the presence of potassium hydroxide to give II (Chart 2). However, it is difficult to rationalize the formation of the intermediate IIb.

Further work is in progress to elucidate the mechanism of this reaction.

Experimental

DMF was prepared by distillation from calcium hydride and was stored over molecular sieve 4A. All melting points are uncorrected. IR spectra were recorded on an IRA-2 spectrophotometer. PMR spectra were taken on a Hitachi R-22 spectrometer at 90 MHz or a JNM-MH-100 spectrometer at 100 MHz using tetramethylsilane as an internal standard. Mass spectra were measured with a JEOL model JMS-01SG spectrometer.

Reaction of 2-Nitronaphthalene (I) with Malononitrile (Table I). Typical Procedure——A suspension of malononitrile (0.03 mol) and KOH (0.03 mol) in DMF (20 ml) was stirred at room temperature until it became clear. A solution of I (0.01 mol) in DMF (10 ml) was then added dropwise with stirring, and the whole was stirred at room temperature for 24 hr. The reaction mixture was poured into ice-water. The precipitate was collected, washed with aq.AcOH and ice-water, and recrystallized from aq.MeOH to yield the potassium salt (II: 2.33 g, 78%) of 1,1-dicyano-2-hydroxy-2-(1-cyano-2-naphthylamino)ethylene as colorless feathery crystals, mp 298° (dec.). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3320 (>NH), 2185, 2160 (CN). Its IR spectrum was identical with that of a specimen prepared by the following method.

Preparation of II. i) 2-Ethoxycarbonylaminonaphthalene-1-carbonitrile——Ethyl chloroformate (1.56 g) was added dropwise to a solution of 2-aminonaphthalene-1-carbonitrile[2] (2 g) in pyridine (20 ml). The mixture was allowed to stand overnight, and the pyridine was removed *in vacuo*. The residue was washed with water and dried. Recrystallization from ether–petr.ether gave 2-ethoxycarbonylaminonaphthalene-1-carbonitrile (2 g, 70%) as colorless needles, mp 147°. *Anal.* Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.79; H, 4.96; N, 11.67. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3320 (>NH), 2205 (CN), 1705 (>C=O). PMR ($CDCl_3$) δ: 1.38 (3H, t, $J=9.2$ Hz, $-\mathrm{C\underline{H}_3}$), 4.36 (2H, q, $J=9.2$ Hz, $-\mathrm{C\underline{H}_2{-}CH_3}$), 7.52 (1H, br.s, NH), 7.36—8.52 (6H, m, aromatic H). MS *m/e*: 240 (M^+).

ii) **Reaction of 2-Ethoxycarbonylaminonaphthalene-1-carbonitrile with Malononitrile**——A suspension of malononitrile (447 mg) and KNH_2 (370 mg) in DMF (10 ml) was stirred at room temperature until it became clear. 2-Ethoxycarbonylaminonaphthalene-1-carbonitrile (800 mg) was then added, and the mixture was heated at 100° for 4 hr with stirring. After removal of the solvent *in vacuo*, the residue was washed with ice-water and ether, and then recrystallized from aq.MeOH to provide II (607 mg, 63%) as colorless feathery crystals, mp 298° (dec.).

Hydrolysis of II——a) A suspension of II (596 mg) in 20% HCl (20 ml) was refluxed for 48 hr. The mixture was basified with $NaHCO_3$, and extracted with $CHCl_3$. The extract was recrystallized from ether-petr.ether to give 2-aminonaphthalene (146 mg, 51%) as colorless scales, mp 111° (lit.,[4] 112°), undepressed on admixture with an authentic sample.

b) A suspension of II (1 g) in 20% HCl (50 ml) was refluxed for 3 hr. The crystals were collected, washed with water, and then recrystallized from aq.acetone to yield 3-dicyanomethylene-3,4-dihydro-1H-naphth[2,1-*d*][1,3]oxazin-1-one (III: 496 mg, 59%) as greenish-yellow needles, mp 320° (dec.). *Anal.* Calcd for $C_{15}H_7N_3O_2$: C, 68.96; H, 2.70; N, 16.09. Found: C, 69.41; H, 2.40; N, 16.20. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3280—3240 (>NH), 2200 (CN), 1775 (>C=O). PMR (DMSO-d_6) δ: 7.57 (1H, d, $J=9$ Hz, C_5-H), 7.55—8.12 (3H, m, aromatic H), 8.32 (1H, d, $J=9$ Hz, C_6-H), 9.07 (1H, d, $J=8$ Hz, C_{10}-H), 9.85 (1H, br.s, >NH). MS *m/e*: 261 (M^+).

c) A portion of 50% H_2SO_4 (5 ml) was slowly added to a solution of II (1 g) in DMF (5 ml) with stirring and ice-cooling. After the mixture had been stirred at room temperature for another 2 hr, the mixture was poured onto ice. The precipitate was collected, and washed with water. Recrystallization from aq.acetone provided III (650 mg, 74%), mp 320° (dec.).

Hydrolysis of 3-Dicyanomethylene-3,4-dihydro-1H-naphth[2,1-*d*][1,3]oxazin-1-one (III)——A suspension of III (260 mg) in 20% HCl (10 ml) was refluxed for 55 hr. After work-up as noted in a), 2-aminonaphthalene (130 mg, 91%) was obtained, mp 111°.

Reaction of III with Amines: General Procedure——A solution of III (500 mg) and an amine (2.3 mmol) in pyridine (5 ml) was refluxed for 3 hr. After removal of the pyridine *in vacuo*, the residue was poured into ice-water, then the crystals were collected, washed with water, and dried. Each benzo[*f*]quinazoline (IVa—d) was recrystallized from the solvent listed in Table II. Table III lists the spectral data of IV.

Reaction of II with Acetic Anhydride——A solution of II (1 g) and acetic anhydride (2 ml) in AcOH (5 ml) was refluxed for 3 hr. After removal of the solvent *in vacuo*, the residue was poured into ice-water. The crystals were collected, washed with water, and then recrystallized from aq.EtOH to give 2-acetoaminonaphthalene-1-carbonitrile (225 mg, 36%) as colorless needles, mp 159°; this product was identical with an authentic sample.[2]

Preparation of Pyridinium Salt (IIa) of 1,1-Dicyano-2-hydroxy-2-(1-cyano-2-naphthylamino)ethylene——Conc.HCl (3 ml) was slowly added to a suspension of II (1.19 g) in pyridine. The reaction mixture was allowed to stand at room temperature overnight. The pyridine was evaporated off *in vacuo*, and the residue was washed with ice-water, then recrystallized from acetone to yield IIa (1.04 g, 77%) as colorless needles, mp 167° (dec.). *Anal.* Calcd for $C_{20}H_{13}N_5O$: C, 70.78; H, 3.86; N, 20.64. Found: C, 70.90; H, 3.63; N, 20.53. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3370 (>NH), 2880—2400 (>N$^+$H), 2170, 2155 (CN).

Conversion of IIa to II——A solution of IIa (500 mg) and AcOK (440 mg) in MeOH (20 ml) was refluxed for 30 min. After removal of the MeOH *in vacuo*, the residue was washed with ice-water, and then recrystallized from aq.MeOH to yield II (450 mg, 98%), mp 298° (dec.).

Benzoylation of II——A suspension of II (2 g) in $CHCl_3$ was heated to effect azeotropic dehydration. The compound was suspended in pyridine (20 ml), and benzoyl chloride (2.5 g) was added dropwise to this suspension under ice-cooling. After the resulting mixture had been allowed to stand overnight, it was poured into ice-water. The precipitate was collected, and successively washed with ice-water and ether. Fractional crystallization from acetone-petr.benzin gave colorless prisms (582 mg, 20%), as the less soluble compound (V), and colorless needles (670 mg, 30%), as the more soluble one (IIa). Pyridinium salt (V) of 1,1-dicyano-2-hydroxy-2-(N-benzoyl-1-cyano-2-naphthylamino)ethylene, mp 164° (dec.). *Anal.* Calcd for $C_{27}H_{17}N_5O_2$: C, 73.13; H, 3.83; N, 15.80. Found: C, 73.29; H, 3.73; N, 16.03. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 2215, 2180, 2160 (CN), 1670 (>C=O).

Benzoylation of IIa——Benzoyl chloride (560 mg) was added to a solution of IIa (678 mg) in pyridine (3 ml) under ice-cooling. The mixture was allowed to stand overnight. After removal of the solvent *in vacuo*, the residue was successively washed with ice-water and ether, and then dried. Recrystallization from MeOH gave V (360 mg, 40%), mp 164° (dec.).

Hydrolysis of V——a) A portion of 50% H_2SO_4 (3 ml) was added dropwise to a stirred solution of V (500 mg) in DMF (5 ml) under ice-cooling. The mixture was stirred at room temperature for another 30 min. The reactants were poured into ice-water and extracted with ether. Removal of the ether gave 2-benzoylaminonaphthalene-1-carbonitrile (158 mg, 52%), mp 210—211° (from ether), colorless needles. This product was identical with an authentic sample prepared from 2-aminonaphthalene-1-carbonitrile.[2] The mother liquor from ether extraction was basified with 20% K_2CO_3, and extracted with $CHCl_3$. The $CHCl_3$ layer was evaporated to dryness to give pyridine. The melting point of its picrate, mp 166° (lit.,[5] mp 167°), was not depressed by admixture with an authentic sample.

b) A suspension of V (100 mg) in 20% HCl (10 ml) was refluxed for 40 hr. The mixture was basified with $NaHCO_3$, and extracted with $CHCl_3$. Removal of the $CHCl_3$ gave 2-aminonaphthalene (30 mg, 93%), mp 111° (from ether–petr.ether). The mother liquor from $CHCl_3$ extraction was acidified with 10% HCl, and then extracted with ether. Removal of the ether by evaporation gave bezoic acid (23 mg, 84%), mp 122°.

Reaction of II with Allyl Bromide——A mixture of II (2 g) and allyl bromide (4 ml) in DMF (20 ml) was stirred at 100—110° for 3 hr. After removal of the DMF *in vacuo*, the residue was added to ice, and the precipitate was collected and dried. Recrystallization from ether gave 2-allylaminonaphthalene-1-carbonitrile (605 mg, 45%) as pale yellow scales, mp 91.5°. *Anal.* Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.47; H, 5.75; N, 13.70. IR ν_{max}^{KBr} cm^{-1}: 3360 (>NH), 2180 (CN). PMR ($CDCl_3$) δ: 3.96 (2H, m, $-C\underline{H}_2CH{=}CH_2$), 5.14 (1H, d.d, $J=3.4$ and 1.6 Hz, ${}^{-CH_2}_{H}\!>\!C{=}C\!<_{\underline{H}}$), 5.30 (1H, d.d, $J=10.8$ and 1.6 Hz, ${}^{-CH_2}_{H}\!>\!C{=}C\!<^{\underline{H}}$), 5.05—5.25 (1H, br.s, $>N\underline{H}$), 5.72—6.12 (1H, m, $-C\underline{H}{=}CH_2$), 6.88 (1H, d, $J=9$ Hz, C_3–H), 7.20—7.95 (5H, m, aromatic H). MS *m/e*: 218 (M^+).

Reaction of II with Dimethyl Sulfate——A mixture of II (2 g) and dimethyl sulfate (4 ml) in CH_3CN (40 ml) was refluxed for 3 hr. After removal of the solvent *in vacuo*, the residue was basified with $NaHCO_3$. The deposited crystals were collected, washed with water, dried, and then extracted with $CHCl_3$. The $CHCl_3$–insoluble residue was recrystallized from acetone to give III (104 mg, 6%), mp 319°. The $CHCl_3$ extract was chromatographed on silica gel. The first fraction eluted with $CHCl_3$ gave 2-methylaminonaphthalene-1-carbonitrile (207 mg, 18%), pale yellow needles, mp 142° (from ether). *Anal.* Calcd for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53; N, 15.38. Found: C, 79.10; H, 5.51; N, 15.67. IR ν_{max}^{KBr} cm^{-1}: 3360 (>NH), 2180 (CN). PMR ($CDCl_3$) δ: 2.95 (3H, s, $-C\underline{H}_3$), 5.07 (1H, br.s, >NH), 6.84 (1H, d, $J=9$ Hz, C_3–H), 7.16—7.92 (5H, m, aromatic H). MS *m/e*: 182 (M^+). The second fraction eluted with $CHCl_3$ afforded 2-aminonaphthalene-1-carbonitrile (373 mg, 34%), colorless scales, mp 131° (from $CHCl_3$). This product was identical with an authentic sample.[2)]

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References and Notes

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