Studies on Conjugated Nitriles. VI.[1] Reaction of 2-Methylquinoline and Related Compounds with Acyl Cyanides

Masanori SAKAMOTO,* Mitsuaki ABE, and Keitaro ISHII

Meiji College of Pharmacy, 1–35–23 Nozawa, Setagaya-ku, Tokyo 154, Japan. *Received July 23, 1990*

The reactions of 2-methylquinoline (7), 2-methylbenzothiazole (25), and related compounds 8—11 and 26—30 with benzoyl cyanide (1) or 4-nitrobenzoyl cyanide (2) proceeded *via* the cyanohydrin derivatives to afford the corresponding *C*-acylated products 12—17 and 31—36.

Keywords azine ring; azole ring; azoline ring; benzoyl cyanide; 4-nitrobenzoyl cyanide; *C*-acylation; cyanohydrin

The reaction of aldimines or ketimines with benzoyl cyanide (**1**) generally affords Reissert-type compounds.[2] Previously, we reported that the reaction of *N*-(1-phenylalkylidene)benzylamine **3a**, **b** and 1-alkyl-3,4-dihydroisoquinolines **5a—d** with 4-nitrobenzoyl cyanide (**2**) gave 4,5-dihydropyrrole derivatives **4a**, **b**[3] and **6a—d**,[4] respectively. The reactions presumably proceed initially by nucleophilic addition of **3** and **5** in the enamine form to **2**, affording the cyanohydrin intermediates, followed by cyclization to the adducts **4** and **6** (Chart 1).

Therefore, it is of interest to compare the reactivity of the imino moiety in a heteroaromatic system with that of compounds **3** and **5**. The subject of the present paper is the reaction of compounds **7—11**, possessing an imino moiety in a six-membered aromatic ring, with **1** and **2**.

The reaction of 2-methylquinoline (**7**) with **1** in refluxing xylene afforded a 22:1[5] mixture of (*Z*)-1,2-dihydro-2-benzoylmethylenequinoline (**12A**)[6] and 2-benzoylmethylquinoline (**12C**)[6] in 22% yield. Three tautomeric structures can be considered in the product **12**: the enamine form **12A**, the enol form **12B**, and the keto form **12C**. The structure of **12** was determined from a comparison of its ultraviolet (UV),[7] infrared (IR), and proton nuclear magnetic resonance (^{1}H-NMR) spectral data with literature values.[6a,b] The following key signals in the ^{13}C-NMR spectrum also supported these structures: a doublet at 89.9 ppm and a triplet at 48.8 ppm due to the carbon atom positioned α to the carbonyl group for **12A** and for **12C**, a singlet at 154.2 ppm due to the C-2 carbon atom, and two singlets at 184.1 and 195.6 ppm due to the carbonyl carbon atom for **12A** and for **12C**, respectively (Chart 2).

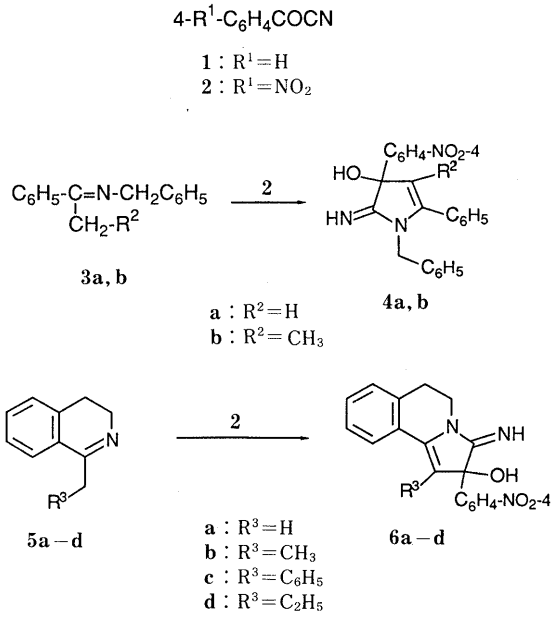
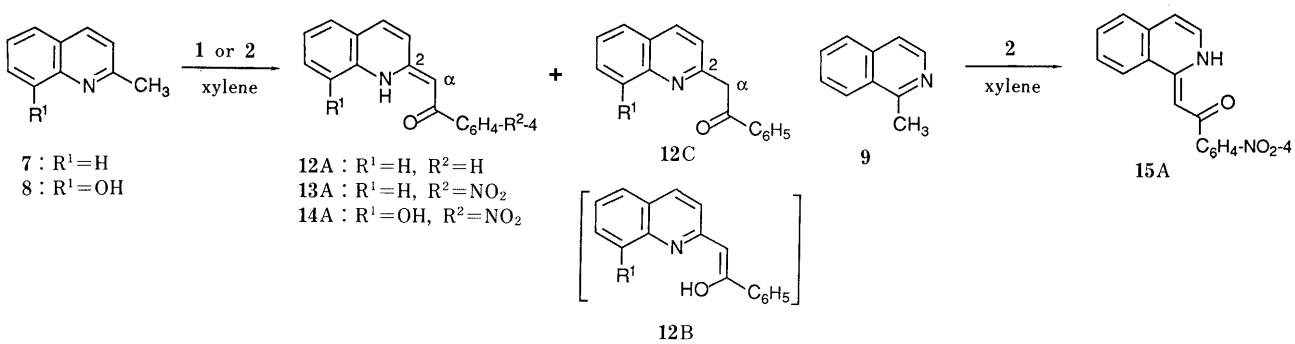


Chart 1



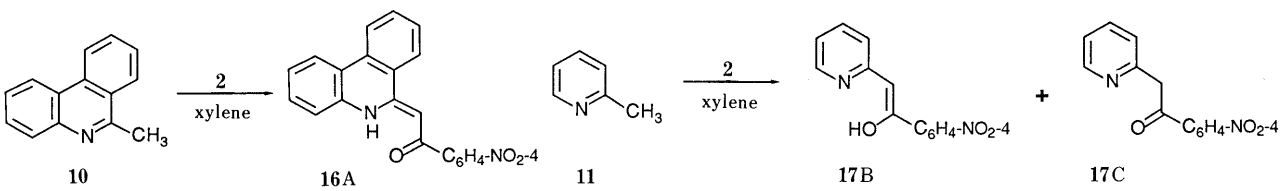


Chart 2

TABLE I. Results and Characterization for Compounds **12**—**17**

Substrate	Method[a]	Time (h)	Product	Yield (%)	mp (°C) (Solv.)[b]	Mol. Formula	Analysis (%) Found C	Found H	Found N	Calcd C	Calcd H	Calcd N
7	II	15	**12**	22	117—118 (PA) [116—117][c]	$C_{17}H_{13}NO$	82.36	5.05	5.63	82.57	5.30	5.66
7	I	15	**13**	48	210—211 (AC)	$C_{17}H_{12}N_2O_3$	70.13	3.84	9.59	69.85	4.14	9.59
8	I	6	**14**	7	293—294 (AC)	$C_{17}H_{12}N_2O_4$	66.16	3.71	9.09	66.23	3.92	9.09
9	I	12	**15**	48	239—240 (AC)	$C_{17}H_{12}N_2O_3$	69.55	3.96	9.73	69.85	4.14	9.59
10	I	15	**16**	34	254—255 (DMF)	$C_{21}H_{14}N_2O_3$	73.97	3.85	8.21	73.67	4.12	8.18
11	II	4	**17**	11	176—177 (BE)	$C_{13}H_{10}N_2O_3$	64.73	3.95	11.53	64.46	4.16	11.57

a) See the experimental section. *b*) PA = petroleum ether, AC = acetone, DMF = dimethylformamide, and BE = benzene. *c*) Ref. 6*b*.

TABLE II. Spectral Data for **12**—**17** and **20**—**22**

Compd.	UV $\lambda_{max}^{CHCl_3}$ nm (log ε)	IR ν_{max}^{KBr} cm^{-1} N–H	IR C=O	^{1}H-NMR δ: ppm CαH (**A** or **B**)	CαH$_2$ (**C**)	NH or OH
12	439 (3.76), 456 (3.77)	3440	1634	6.07 (**A**)	4.84	15.7[f]
	427 (4.49), 453 (4.45)[a]		1636[d]			
	[428 (4.51), 453 (4.45)][a,b]		[1639][b,d]	[5.98][b]	[4.75][b,f]	
13	449 (4.41), 466 (4.40)	3440	1632	6.45 (**A**)	—[e]	15.8[g]
	455 (4.27), 476 (4.28)[c]					
14	460 sh (4.29), 476 (4.31)[c]	3450	1634	6.43 (**A**)	—[e]	15.7[h]
15	447 (4.39)	3460	1608	7.04 (**A**)	—[e]	16.1[i]
16	448 (4.39)	3460	1595	7.29 (**A**)	—[e]	—[e,h]
				6.81 (**A**)	—[e]	16.1[f]
17	380 (4.22)	3450 (O–H)	1627 (C=C)	6.19 (**B**)	4.67	15.7[f]
20	403 (4.13), 424 (4.16)	3450	1602	6.87 (**A**)	—[e]	15.1[f]
21	403 (4.09), 427 (4.14)	3440	1602	6.83 (**A**)	—[e]	14.8[f]
22	392 (3.75)	3450 (O–H)	1638 (C=C)	6.16 (**B**)	—[e]	15.5[f]

a) In EtOH. *b*) Ref. 6*b*. *c*) In DMSO. *d*) Nujol. *e*) Not detectable. *f*) In $CDCl_3$, r.t. *g*) In DMSO-d_6, 70 °C. *h*) In DMSO-d_6, r.t. *i*) In DMSO-d_6, 80 °C.

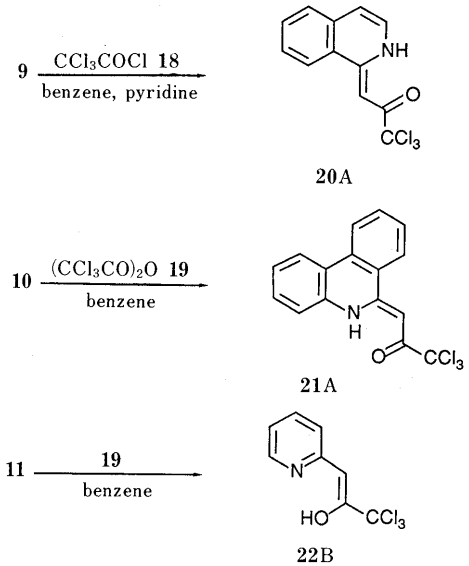


Chart 3

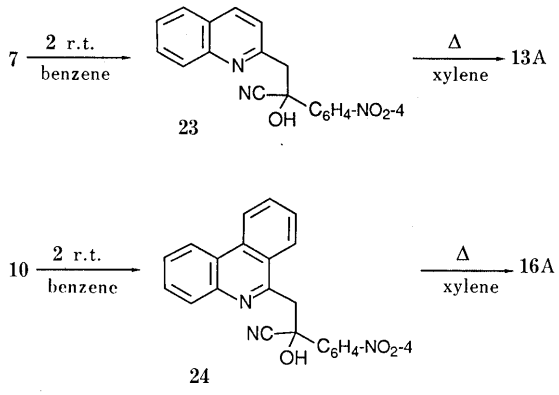


Chart 4

Similarly, the reactions of **7**, 8-hydroxy-2-methylquinoline (**8**), 1-methylisoquinoline (**9**), 6-methylphenanthridine (**10**), and 2-methylpyridine (**11**) with **2** afforded *C*-acylated compounds **13A**,[8] **14A**[8] **15A**,[8] **16A**,[8] and **17B** and **17C** (13 : 1),[5] respectively. The structures of the products **13**—**16** were deduced from a comparison of their spectral data with those of **12**. The structure of **17B** was confirmed by comparison of the spectral data with those of 2-phenacylpyridine.[6c,9] The results of the reaction, the characterization, and the relevant spectral data for **12**—**17** are summarized in Tables I and II.

Further evidence for the structures of **15**—**17** was obtained from their reactions with **9**—**11** and trichloracetyl chloride (**18**) or trichloroacetic anhydride (**19**), *C*-acylation agents for imines of this type,[10] which afforded **20A**[8] (2%), **21A**[8] (13%), and **22B**[8] (5%), respectively. The spectral data for **20**—**22** also supported the *C*-acylated structures of **15**—**17** (Chart 3). The relevant spectral data for **20**—**22** are listed in Table II.

On the other hand, the reactions of **7** and **10** with **2** in benzene at room temperature (r.t.) gave the cyanohydrins **23** (29%) and **24** (36%), which were transformed by

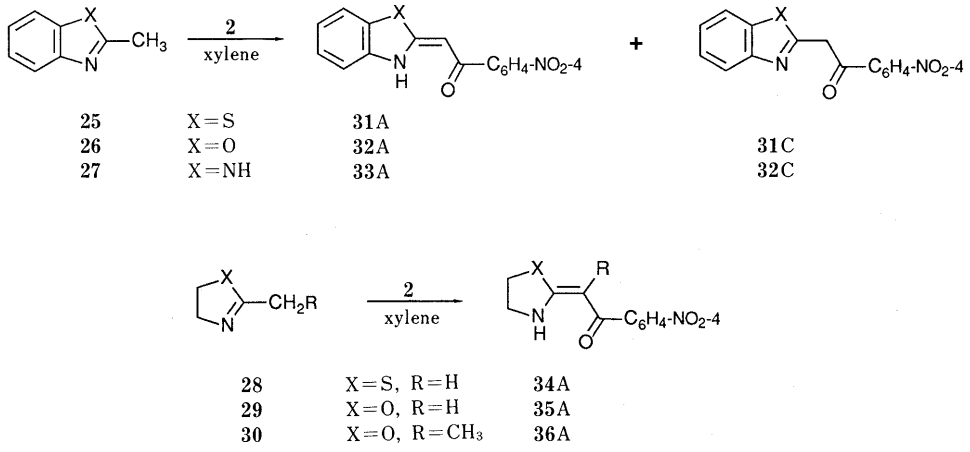


Chart 5

TABLE III. Results and Characterization for Compounds **31**—**36**

Substrate	Time (h)	Product	Yield (%)	mp (°C) (Solv.)[a]	Mol. Formula	Analysis (%) Found C	Found H	Found N	Calcd C	Calcd H	Calcd N
25	8	**31**	17	224—225 (AC)	$C_{15}H_{10}N_2O_3S$	60.31	3.22	9.38	60.39	3.38	9.39
26	25	**32**	20	248—249 (AC)	$C_{15}H_{10}N_2O_4$	63.92	3.35	9.93	63.83	3.57	9.93
27	6	**33**	9	165—166 (DMF)	$C_{15}H_{11}N_3O_3$	64.15	3.74	15.05	64.05	3.94	14.94
28	72	**34**	37	226—227 (AC)	$C_{11}H_{10}N_2O_3S$	52.59	4.00	11.13	52.80	4.03	11.20
29	12	**35**	39	263—264 (AC)	$C_{11}H_{10}N_2O_4$	56.27	4.20	12.05	56.41	4.30	11.96
30	72	**36**	30	179—180 (AC)	$C_{12}H_{12}N_2O_4$	57.89	4.84	11.28	58.06	4.87	11.29

a) See footnote to Table I.

TABLE IV. Spectral Data for **31**—**36**

Compd.	UV $\lambda_{max}^{CHCl_3}$ nm (log ε)	IR ν_{max}^{KBr} cm^{-1} N–H	IR C=O	^{1}H-NMR δ: ppm CαH (A)	CαH$_2$ (C)	NH or OH
31	302 (3.97), 387 (4.44)	3460	1626	6.88	5.12	—[b,c]
32	375 (4.35), 378 (4.17)[a]	3450	1637	6.70	4.96	—[b,d]
33	331 (4.18),[a] 412 (4.16)[a]	3440	1616	6.15	—[b]	—[b,e]
34	273 (4.00), 370 (4.00)	3460	1612	5.97	—[b]	10.73[f]
35	268 (4.26), 352 (4.07)	3450	1625	5.58	—[b]	9.87[d]
36	296 (4.73), 350 (3.38)	3440	1638			10.29[g]

a) In DMSO. *b*) Not detectable. *c*) In DMSO-d_6, 50 °C. *d*) In DMSO-d_6, 80 °C. *e*) In DMSO-d_6, 40 °C. *f*) In $CDCl_3$, r.t. *g*) In DMSO-d_6, r.t.

refluxing in xylene to **13A** and **16A**, respectively. The structures of **23** and **24** were determined from the spectral data. In particular, the ^{1}H-NMR spectra for **23** and **24** showed two doublets at 3.66 and 3.94 ppm and 3.96 and 4.58 ppm due to the methylene protons, respectively (Chart 4).

The reactions of the six-membered aromatic nitrogen ring system in **7**—**11** with **1** and **2** gave the corresponding *C*-acylated compounds. Furthermore, the investigated the reactions of the azole and azoline ring systems in **25**—**30**, bearing one heteroatom at the 3-position to the nitrogen atom, with **2**.

Compounds **25**—**30** were refluxed with **2** in xylene to afford the corresponding *C*-acylated compounds **31A** and **31C** (16 : 1),[5] **32A** and **32C** (1.8 : 1),[5] **33A**,[8] **34A**,[8] **35A**,[8] and **36A**,[8] respectively (Chart 5). The results, the characterization, and selected spectral data for the products **31**—**36** are summarized in Table III and IV. The tautomeric

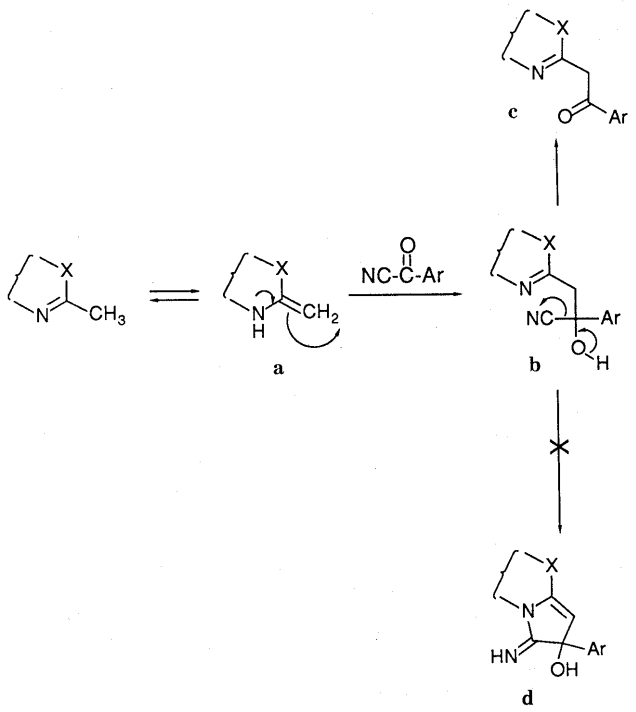


Chart 6

structure A and *E*/*Z*-configuration for the products **31**—**36** were deduced from a comparison of their spectral data with those of compounds **12**—**17**, 2-methylenebenzothiazoline,[11a] and 2-methylenethiazoline derivatives.[11b]

The proposed mechanism for the formation of *C*-acylated compounds is shown in Chart 6. The enamine form **a** of the imines undergoes addition to **1** and **2**, leading to the cyanohydrin intermediate **b**, followed by elimination of hydrogen cyanide to give the *C*-acylated compound **c**. In contrast to the reaction of **3**[3] and **5**[4] with **2**, the reaction of **7**—**11** and **25**—**30** with **2** did not afford the cyclic product **d**. The nucleophilicity of the imine nitrogen in **7**—**11** and **25**—**30** is not enough to permit attack on the cyano group, leading to **d**, since the nitrogen atom is incorporated into the aromatic system and/or may be influenced by the inductive effect of the heteroatom (X) (Chart 6).

Experimental

Melting points were measured with a Yanaco MP-3 apparatus and are uncorrected. UV spectra were recorded on a Hitachi 124 spectrometer and IR spectra on a Hitachi 215 spectrometer. ^{1}H-NMR spectra were obtained with a JEOL PS-100 (PS), a JEOL JNM-EX270 (EX), or a JEOL GX-400 (GX) spectrometer and ^{13}C-NMR spectra were run on an EX or a GX spectrometer using tetramethylsilane as the internal standard. Mass spectra (MS) were taken on a JEOL JMS-D300 spectrometer. Column chromatography (CC) was performed with Kanto silica gel, 80—100 mesh.

4-Nitrobenzoyl cyanide (**2**) was prepared by the method of Dornow and Grabhofer.[12]

General Procedure for the Reactions of the Azines 7—11 and Acyl Cyanides 1 and 2 A solution of an azine (2 mmol) and an acyl cyanide (2 mmol) in anhydrous xylene (30 ml) was heated under reflux for an appropriate time (Table I). Method I: After cooling, the resulting precipitates were collected by filtration. Method II: After removal of the solvent *in vacuo*, the residue was purified by CC ($CHCl_3$ as an eluent). In both cases, the crude product was purified was purified by recrystallization. The results, the characterization, and UV spectral data are summarized in Tables I and II.

(*Z*)-1,2-Dihydro-2-benzoylmethylenequinoline (**12A**) and 2-Benzoylmethylquinoline (**12C**)[6] (22 : 1)[5]: Yellow needles. ^{1}H-NMR ($CDCl_3$, r.t., GX) δ: 4.84 (2H, s, CH_2 for **12C**), 6.07 (1H, s, HC=C(2) for **12A**), 6.85 (1H, d, J=9.2 Hz, H-C(3)), 7.22—7.27, 7.42—7.53, 7.94—7.97 (9H, 3m, H-Ar), 7.63 (1H, d, J=9.2 Hz, H-C(4)), 15.7 (1H, br s, NH). ^{13}C-NMR ($CDCl_3$, r.t., GX) δ: 48.8 (t, CH_2 for **12C**), 89.9 (d, C=C(2) for **12A**), 118.2 (d, C(3)), 122.3, 123.7, 127.6, 130.4, 131.0 (5d, 4C in Ar, 1C in Ph), 123.3 (s, C(4a)), 126.7, 128.3 (2d, 4C in Ph), 136.2 (d, C(4)), 137.8 (s, 1C in Ph), 139.8 (s, C(8a)), 154.2 (s, C(2)), 184.1 (s, CO). MS *m/z*: 247 (M^+), 219 ($M^+ -28$), 105 ($PhCO^+$).

(*Z*)-1,2-Dihydro-2-(4′-nitrobenzoylmethylene)quinoline (**13A**): Red needles. IR (KBr): 3440 (N–H), 1630 (C=O), 1531, 1341 cm^{-1} (NO_2). ^{1}H-NMR (DMSO-d_6, 70°C, GX) δ: 6.45 (1H, s, HC=C(2), D_2O-erasable), 7.22 (1H, d, J=9.0 Hz, H-C(3)), 7.42 (1H, ddd, J_1=8, J_2=7.1, J_3=1.2 Hz, H-C(7)), 7.68 (1H, ddd, J_1=8.3, J_2=7.1, J_3=1.2 Hz, H-C(6)), 7.75 (1H, d, J= 8.3 Hz, H-C(5)), 7.80 (1H, dd, J_1=8, J_2=1.2 Hz, H-C(8)), 8.09 (1H, d, J=9.0 Hz, H-C(4)), 8.17, 8.29 (4H each, d, J=9.0 Hz, $C_6H_4NO_2$),15.8 (1H, br s, NH, D_2O-erasable). MS *m/z*: 292 (M^+), 170 ($M^+ -122$).

(*Z*)-1,2-Dihydro-8-hydroxy-2-(4′-nitrobenzoylmethylene)quinoline (**14A**): Orange needles. IR (KBr): 3450 (N–H), 1634 (C=O), 1524, 1340 cm^{-1} (NO_2). ^{1}H-NMR (DMSO-d_6, r.t., GX) δ: 6.43 (1H, s, HC=C(2), D_2O-erasable), 7.12—7.27 (4H, m, H-Ar), 8.02 (1H, d, J=9.3 Hz, H-C(4)), 8.18, 8.31 (4H each, d, J=9.0 Hz, $C_6H_4NO_2$), 10.89 (1H, br s, OH, D_2O-erasable), 15.7 (1H, br s, NH, D_2O-erasable). ^{13}C-NMR (DMSO-d_6, r.t., EX) δ: 89.9 (d, C=C(2)), 114.6, 117.9, 122.2, 124.4 (4d, 4C in Ar), 123.5, 127.5 (2d, 4C in $C_6H_4NO_2$), 124.1, 126.7, 145.5, 148.2 (5s, 2s at 145.5, 3C in Ar, 2C in $C_6H_4NO_2$), 152.7 (s, C(2)), 179.5 (s, CO). MS *m/z*: 308 (M^+), 158 ($M^+ -150$), 150 ($COC_6H_4NO_2^+$).

(*Z*)-1,2-Dihydro-1-(4′-nitrobenzoylmethylene)isoquinoline (**15A**): Red needles. IR (KBr): 3460 (N–H), 1608 (C=O), 1558, 1342 cm^{-1} (NO_2). ^{1}H-NMR (DMSO-d_6, 80°C, GX) δ: 7.04 (1H, s, HC=C(1), D_2O-erasable), 7.14 (1H, d, J=6.6 Hz, H-C(4)), 7.62—7.67 (1H, m, H-C(7)), 7.79—7.82 (3H, m, H-C(3), H-C(5), H-C(6)), 8.26, 8.31 (4H, each d, J=8.8 Hz, $C_6H_4NO_2$), 8.57 (1H, d, J=8.1 Hz, H-C(8)), 16.1 (1H, br s, NH, D_2O-erasable). MS *m/z*: 292 (M^+).

(*Z*)-5,6-Dihydro-6-(4′-nitrobenzoylmethylene)phenanthridine (**16A**): Red needles. IR (KBr): 3460 (N–H), 1595 (C=O), 1556, 1342 cm^{-1} (NO_2). ^{1}H-NMR (DMSO-d_6, r.t., EX) δ: 7.29 (1H, s, HC=C(6)), 7.54, 7.73 7.85, 8.03 (4H, 4m with t-character, J=8 Hz, H-C(2), H-C(3), H-C(8), H-C(9)), 7.75, 8.63, 8.76, 8.84 (4H, 4d, J=8 Hz, H-C(1), H-C(4), H-C(7), H-C(10)), 8.40, 8.49 (4H, each d, J=8.9 Hz, $C_6H_4NO_2$). ^{1}H-NMR ($CDCl_3$, r.t., GX) δ: 6.81 (1H, br s, HC=C(6)), 7.38—7.44 (1H, m), 7.52—7.62 (2H, m), 7.67, 7.85 (2H, 2m with t-character, J=7.5 Hz), 8.17 (2H, m with d-character), 8.28—8.34 (4H, m), 8.44 (1H, m with d-character), 16.1 (1H, br s, NH). MS *m/z*: 342 (M^+), 220 ($M^+ -122$).

(*Z*)-2-(2′-Hydroxy-2′-(4″-nitrophenyl)vinyl)pyridine (**17B**) and 2-(4′-Nitrobenzoylmethyl)pyridine (**17C**) (13 : 1)[5]: Yellow needles. IR (KBr): 3450 (O-H), 1627 (C=C), 1518, 1336 cm^{-1} (NO_2). ^{1}H-NMR ($CDCl_3$, r.t., EX) δ: 4.67 (2H, s, CH_2 for **17C**), 6.19 (1H, s, H-C(1′) for **17B**), 7.09 (1H, ddd, J_1=7.3, J_2=5.0, J_3=1.0 Hz, H-C(5)), 7.15 (1H, d, J=7.9 Hz, H-C(3)), 7.65—7.73 (1H, t with fine splitting, J=8 Hz, H-C(4)), 7.99, 8.26 (4H, each d, J=8.9 Hz, $C_6H_4NO_2$), 8.35 (1H, d, J=5.0 Hz, H-C(6)), 15.7 (1H, br s, OH). ^{13}C-NMR (DMSO-d_6, r.t., GX) δ: 47.8 (t, CH_2 for **17C**) 96.1 (d, C(1′) for **17B**), 119.4, 122.2 (2d, C(3), C(5)), 123.3, 126.0 (2d, 4C in $C_6H_4NO_2$), 138.0 (d, C(4)), 142.2, 147.5 (2s, 2C in $C_6H_4NO_2$), 143.8 (d, C(6)), 156.8 (s, C(2)), 161.2 (s, C(2′) for **17B**), 196.2 (s, CO for **17C**). MS *m/z*: 242 (M^+).

Reactions of the Azines 9—11 with Trichloroacetyl Chloride (18) or Trichloroacetic Anhydride (19) A solution of **18** (340 mg, 2.00 mmol) in anhydrous benzene (20 ml) was added dropwise to a stirred solution of **9** (286 mg, 2.00 mmol) in anhydrous benzene (20 ml) and pyridine (174 mg, 2.2 mmol). The reaction mixture was stirred for 24 h at room temperature. The resulting precipitates were filtered, and the filtrate was dried over $MgSO_4$. After removal of the solvent *in vacuo*, the residue was purified by CC (ethyl acetate). Recrystallization from benzene afforded 10 mg (2%) of (*Z*)-1,2-dihydro-1-trichloroacetylmethylenisoquinoline (**20A**) as yellow needles, mp 205—206 °C. *Anal.* Calcd for $C_{12}H_8Cl_3NO$: C, 49.95; H, 2.79; N, 4.85. Found: C, 49.74; H, 2.59; N, 4.83. IR (KBr): 3450 (N–H), 1602 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$, r.t., GX) δ: 6.87 (1H, s, HC=C(1)), 7.03 (1H, d, J=6.7 Hz, H-C(4)), 7.46—7.52 (1H, m, $W_{1/2}$=13.5 Hz, H-C(3)), 7.63 (1H, t with fine splitting, J=8 Hz, H-C(7)), 7.69 (1H, d, J=7.3 Hz, H-C(5)), 7.78 (1H, t with fine splitting, J=7 Hz, H-C(6)), 8.22 (1H, d, J=8.5 Hz, H-C(8)), 15.1 (1H, br s, NH). MS *m/z*: 291 ($M^+ +4$), 289 ($M^+ +2$), 287 (M^+), 170 ($M^+ -117$).

A solution of **19** (618 mg, 2.00 mmol) in anhydrous benzene (20 ml) was added dropwise to a stirred solution of **10** (386 mg, 2.00 mmol) in anhydrous benzene (20 ml). The reaction mixture was stirred for 12 h at room temperature. The resulting precipitates were filtered and the filtrate was washed with saturated $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent *in vacuo*, recrystallization of the residue from benzene afforded 85 mg (13%) of (*Z*)-5,6-dihydro-6-trichloroacetylmethylenephenanthridine (**21A**) as yellow needles, mp 231—232 °C. *Anal.* Calcd for $C_{16}H_{10}Cl_3NO$: C, 56.78; H, 2.98; N, 4.14. Found: C, 56.83; H, 2.73; N, 4.09. IR (KBr): 3440 (N–H), 1602 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$, r.t., GX) δ: 6.83 (1H, s, HC=C(6), D_2O-erasable), 7.39, 7.53, 7.61, 7.81 (4H, 4t, J=8 Hz, H-C(2), H-C(3), H-C(8), H-C(9)), 7.42, 8.17, 8.21 (3H, 3d, J=8 Hz, H-C(1), H-C(4), H-C(10)), 8.33 (1H, d, J=7.9 Hz, H-C(7)), 14.8 (1H, br s, NH, D_2O-erasable). ^{13}C-NMR ($CDCl_3$, r.t., GX) δ: 80.1 (d, HC=C(6)), 97.6 (s, CCl_3), 118.6, 122.7, 122.8, 125.1, 125.8, 128.5, 130.3, 133.1 (8d, 8C in Ar), 120.8, 123.8, 132.4, 133.6 (4s, 4C in Ar), 154.9 (s, C(6)), 180.2 (s, CO). MS *m/z*: 341 ($M^+ +4$), 339 ($M^+ +2$), 337 (M^+), 220 ($M^+ -117$).

2-Methylpyridine (**11**) (465 mg, 5.00 mmol) and **19** (1.55 g, 5.00 mmol) were allowed to react, and the reaction mixture was worked up as described above to afford 50 mg (5%) of (*Z*)-2-(2′-hydroxy-2′-trichloroacetylvinyl)-pyridine (**22B**) as yellow needles, mp 153.5—154.5 °C. *Anal.* Calcd for $C_8H_6Cl_3NO$: C, 40.29; H, 2.54; N, 5.87. Found: C, 40.41; H, 2.37; N, 5.86. IR (KBr): 3450 (O–H), 1638 cm^{-1} (C=C). ^{1}H-NMR ($CDCl_3$, r.t., EX) δ: 6.16 (1H, s, H-C(1′)), 6.92 (1H, ddd, J_1=7.3, J_2=5.9, J_3=1.3 Hz, H-C(5)), 7.10 (1H, d, J=8.9 Hz, H-C(3)), 7.64 (1H, ddd, J_1=8.9, J_2=7.3, J_3=1.3 Hz, H-C(4)), 7.91 (1H, d, J=5.9 Hz, H-C(6)), 15.5 (1H, br s, OH). ^{13}C-NMR ($CDCl_3$, r.t., GX) δ: 84.1 (d, C(1′)), 96.5 (s, CCl_3), 116.2, 123.1 (2d, C(3), C(5)), 136.3, 139.3 (2d, C(4), C(6)), 155.8 (s, C(2)), 174.2 (s, C(2′)). MS *m/z*: 241 ($M^+ +4$), 239 ($M^+ +2$), 237 (M^+), 120 ($M^+ -117$), 92 ($M^+ -145$).

Reactions of the Azines 7 and 10 with 2 at Room Temperature A solution of **7** (286 mg, 2.00 mmol) and **2** (344 mg, 2.00 mmol) in anhydrous benzene (30 ml) was stirred at room temperature for 12 h. The resulting precipitates were collected by filtration. Recrystallization from acetone yielded 286 mg (29%) of 2-(2′-cyano-2′-hydroxy-2′-(4″-nitrophenyl)ethyl)quinoline (**23**) as orange prisms, mp 209—210 °C. *Anal.* Calcd for $C_{18}H_{13}N_3O_3$: C, 67.70; H, 4.11; N, 13.16. Found: C, 67.74; H, 3.89; N, 13.19. UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 265 (3.97), 305 (3.59), 318 (3.59). IR (KBr): 3440 (O–H), 1527, 1347 cm^{-1}

(NO_2).[13] ^{1}H-NMR (acetone-d_6, r.t., PS) δ: 3.66, 3.94 (2H, each d, J=17 Hz, 2H-C(1')), 7.4—8.5 (6H, m, H-Ar), 8.02, 8.35 (4H, each d, J=9 Hz, $C_6H_4NO_2$), 8.00—8.34 (1H, br, OH). MS m/z: 292 (M^+ −27).

A solution of **10** (386 mg, 2.00 mmol) and **2** (344 mg, 2.00 mmol) in anhydrous benzene (30 ml) was stirred and worked-up as described above. Recrystallization of the product from acetone yielded 247 mg (36%) of 6-(2'-cyano-2'-hydroxy-2'-(4''-nitrophenyl)ethyl)phenanthridine (**24**) as yellow needles, mp 253—254 °C. *Anal.* Calcd for $C_{22}H_{15}N_3O_3$: C, 71.53; H, 4.09; N, 11.38. Found: C, 71.58; H, 3.89; N, 11.43. UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 256 (4.83), 334 (3.54), 349 (3.46). IR (KBr): 3440 (O–H), 1524, 1344 cm^{-1} (NO_2).[13] ^{1}H-NMR (acetone-d_6, r.t., PS) δ: 3.96, 4.58 (2H, each d, J=17 Hz, 2H-C(1')), 7.7—9.0 (9H, m, H-Ar and OH), 8.12, 8.37 (4H, each d, J=9 Hz, $C_6H_4NO_2$). MS m/z: 342 (M^+ −27), 220 (M^+ −149).

Transformations of the Cyanohydrins 23 and 24 to 12 and 16, Respectively A solution of **23** (31.8 mg, 0.100 mmol) in anhydrous xylene (1 ml) was stirred under reflux for 4 d. After cooling, the resulting precipitates were collected by filtration, yielding **12** quantitatively. A solution of **23** (31.8 mg, 0.100 mmol) in 20% aqueous NaOH (1 ml) was stirred for 12 h at room temperature. The resulting precipitates were collected by filtration, affording **12** quantitatively.

The cyanohydrin **24** (36.9 mg, 0.100 mmol) was treated as described above, affording **16** quantitatively.

General Procedure for the Reactions of the Azoles 25—27 and the Acyl Cyanide 2 A 0.10 M solution of an azole and 1 eq of **2** in anhydrous xylene was refluxed for an appropriate time (Table III). After cooling, the resulting precipitates were collected by filtration, and the crude product was purified by recrystallization. The results, the characterization, and UV spectral data are summarized in Table III and IV.

(*E*)-2-(4'-Nitrobenzoylmethylene)benzothiazoline (**31A**) and 2-(4'-Nitrobenzoylmethyl)benzothiazole (**31C**) (16 : 1)[5]: Orange prisms. IR (KBr): 3460 (N–H), 1626 (C=O), 1517, 1337 cm^{-1} (NO_2). ^{1}H-NMR (DMSO-d_6, 50 °C, EX) δ: 5.12 (2H, s, CH_2 for **31C**, D_2O-erasable), 6.88 (1H, s, HC=C(2) for **31A**, D_2O-erasable), 7.27, 7.44 (2H, each t, J=7.5 Hz, H-C(5), H-C(6)), 7.47—7.59 (1H, m, H-C(7)), 7.88 (1H, d, J=7.5 Hz, H-C(4)), 8.13, 8.31 (4H, each d, J=9 Hz, $C_6H_4NO_2$). MS m/z: 298 (M^+), 270 (M^+ −28), 167 (M^+ −122), 150 ($COC_6H_4NO_2^+$).

(*E*)-2-(4'-Nitrobenzoylmethylene)benzoxazoline (**32A**) and 2-(4'-Nitrobenzoylmethyl)benzoxazole (**32C**) (1.8 : 1)[5]: Yellow needles. IR (KBr): 3450 (N–H), 1637 (C=O), 1525, 1343 cm^{-1} (NO_2). ^{1}H-NMR (DMSO-d_6, 80 °C, GX) δ: 4.96 (2H, s, CH_2 for **32C**, D_2O-erasable), 6.70 (1H, s, HC=C(2) for **32A**, D_2O-erasable), 7.33—7.43, 7.65—7.72 (4H, m, H-Ar), 8.19, 8.30 (4H, each d, J=9.0 Hz, $C_6H_4NO_2$ for **32A**), 8.27, 8.35 (4H, each d, J=8.5 Hz, $C_6H_4NO_2$ for **32C**). MS m/z: 282 (M^+), 150 ($COC_6H_4NO_2^+$).

2-(4'-Nitrobenzoylmethylene)benzimidazoline (**33A**): Red prisms. IR (KBr): 3440 (N–H), 1616 (C=O), 1528, 1338 cm^{-1} (NO_2). ^{1}H-NMR (DMSO-d_6, 40 °C, GX) δ: 6.15 (1H, s, HC=C(2)), 7.17—7.24, 7.47—7.54 (4H, each m, H-Ar), 8.09, 8.29 (4H, each d, J=8.7 Hz, $C_6H_4NO_2$). MS m/z: 281 (M^+), 159 (M^+ −122), 150 ($COC_6H_4NO_2^+$).

General Procedure for the Reactions of the Azolines 28—30 and the Acyl Cyanide 2 A 0.050 M solution of an azoline and 1 eq of **2** in anhydrous ether was stirred at room temperature for an appropriate time (Table III). After removal of the solvent *in vacuo*, the crude product was purified by recrystallization from acetone. The results, the characterization, and UV spectral data are summarized in Tables III and IV.

(*E*)-2-(4'-Nitrobenzoylmethylene)thiazolidine (**34A**): Yellow needles. IR (KBr); 3460 (N–H), 1612 (C=O), 1524, 1343 cm^{-1} (NO_2). ^{1}H-NMR ($CDCl_3$, r.t., EX) δ: 3.33, 4.01 (4H, each t, J=7.6 Hz, 2H-C(4), 2H-C(5)), 5.97 (1H, br s, $W_{1/2}$=13 Hz, HC=C(2)), 7.98, 8.25 (4H, each d, J=8.9 Hz, $C_6H_4NO_2$), 10.73 (1H, br s, $W_{1/2}$=137 Hz, NH). ^{13}C-NMR ($CDCl_3$, r.t., GX) δ: 29.4 (t, C(5)), 49.9 (t, C(4)), 87.4 (d, HC=C(2)), 123.5, 128.0 (2d, 4C in Ph), 145.3, 149.1 (2s, 2C in Ph), 171.5 (s, C(2)), 183.5 (s, CO). MS m/z: 250 (M^+), 222 (M^+ −28).

(*E*)-2-(4'-Nitrobenzoylmethylen)oxazolidine (**35A**): Yellow needles. IR (KBr): 3450 (N–H), 1625 (C=O), 1540, 1341 cm^{-1} (NO_2). ^{1}H-NMR (DMSO-d_6, 80°C, GX) δ: 3.78 (2H, t, J=8.0 Hz, 2H-C(4)), 4.52 (2H, t, J=8.0 Hz, 2H-C(5)), 5.58 (1H, s, HC=C(2), D_2O-erasable), 8.03, 8.21 (4H, each d, J=8.9 Hz, $C_6H_4NO_2$), 9.87 (1H, br s, NH, D_2O-erasable). MS m/z: 234 (M^+), 233 (M^+ −1), 206 (M^+ −28), 112 (M^+ −122).

(*E*)-2-(1'-(4''-Nitrobenzoyl)ethyliden)oxazolidine (**36A**): Yellow needles. IR (KBr): 3440 (N–H), 1638 (C=O), 1542, 1350 cm^{-1} (NO_2). ^{1}H-NMR (DMSO-d_6, r.t., GX) δ: 1.70 (3H, s, Me), 3.80 (2H, td, J_1=8.5, J_2=2.6 Hz, 2H-C(4), J_2 disappeared upon addition of D_2O), 4.54 (2H, t, J=8.5 Hz, 2H-C(5)), 7.59, 8.23 (4H, each d, J=9.0 Hz, $C_6H_4NO_2$), 10.29 (1H, br s, NH, D_2O-erasable). ^{13}C-NMR (DMSO-d_6, r.t., GX) δ: 12.2 (q, Me), 43.8 (t, C(4)), 67.9 (t, C(5)), 81.5 (s, C(1')), 123.3, 128.1 (2d, 4C in $C_6H_4NO_2$), 147.1, 148.7 (2s, 2C in $C_6H_4NO_2$), 169.0 (s, C(2)), 186.7 (s, CO). MS m/z: 248 (M^+), 247 (M^+ −1), 220 (M^+ −28), 150 ($COC_6H_4NO_2^+$).

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