Notes

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Reaction of Aromatic *N*-Oxides with Dipolarophiles. V.[1] 1,3-Cycloaddition of 2-Substituted Pyridine *N*-Oxides with Phenyl Isocyanates

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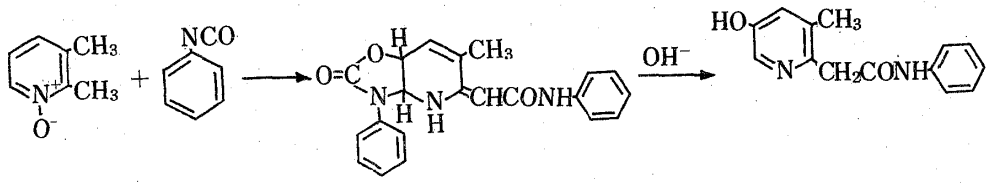
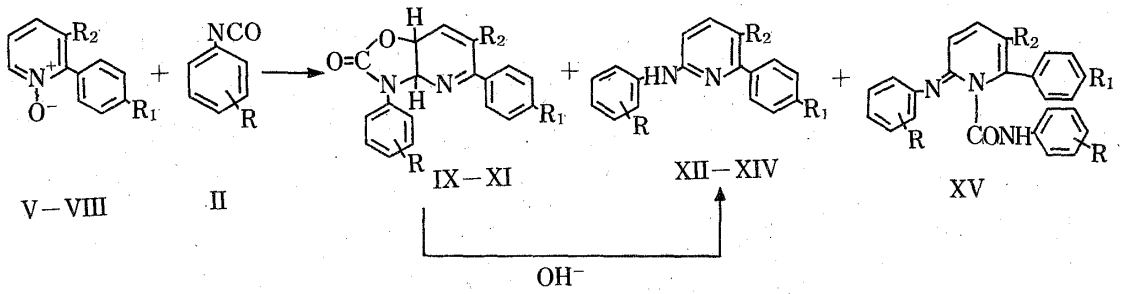
The reaction of 2,3-lutidine *N*-oxide (I) with phenyl isocyanate (IIa) in dimethylformamide at 110°C gave a 1: 2 adduct (IIIa). Under reflux in ethanolic potassium hydroxide, IIIa readily lost a component of IIa and was converted to 5-methyl-6-*N*-phenylcarbamoylmethyl-3-pyridinol (IVa) in 95% yield. 2-Phenylpyridine *N*-oxides (V—VII) reacted with phenyl isocyanates (II) to afford 1: 1 cycloadducts (IX—XI and XII—XIV). The reaction of 2-(*p*-nitrophenyl)pyridine *N*-oxide (VIII) with IIa directly afforded 2-anilino-6-(*p*-nitrophenyl)pyridine derivatives (XIVa and XVa).

Keywords——1,3-dipolar cycloaddition; 2,3-dihydro-2-oxooxazolo[4,5-*b*]pyridine adduct; substituent effect on cycloaddition; 5-methyl-6-*N*-phenylcarbamolylmethyl-3-pyridinol; 2-anilino-6-phenylpyridines

Recent work on the cycloaddition of pyridine *N*-oxides with phenyl isocyanates has shown that the reaction occurs *via* the 2,3-dihydropyridine intermediate.[1,2] In a continuation of our studies on the reaction of 2,3-disubstituted pyridine *N*-oxides with phenyl isocyanates, we succeeded in isolating the 1: 2 adduct (IIIa) from the reaction of 2,3-lutidine *N*-oxide (I) with phenyl isocyanate (IIa).[3] The use of one equivalent of phenyl isocyanate in the above reaction caused a decrease of the yield of the 1: 2 adduct, and attempts to obtain a 1: 1 adduct



I IIa IIIa IVa



V—VIII II IX—XI XII—XIV XV

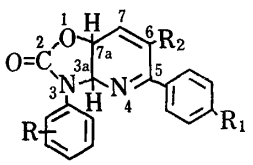
R = H, a; *o*-CH_3, b; *m*-CH_3, c; *p*-CH_3, d; *o*-Cl, e; *m*-Cl, *f*; *p*-Cl, g

Chart 1

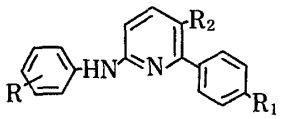
by changing the I/II ratio were not successful. Under reflux in ethanolic potassium hydroxide, IIIa readily lost a component of IIa and was converted to 5-methyl-6-*N*-phenylcarbamoylmethyl-5-pyridinol (IVa) in a high yield of 95%. The elemental analysis of IIIa was in agreement with the empirical formula $C_{21}H_{19}N_3O_3$, and its mass spectrum (MS) indicated that IIIa is a 1:2 adduct of I and IIa. The infrared (IR) spectrum was characteristic of 2-oxooxazolo[4,5-*b*]pyridine.[2] The proton magnetic resonance (^{1}H-NMR) spectrum was consistent with the assignment. The structure of IVa was confirmed by the elemental analysis [$C_{14}H_{14}N_2O_2$] and the MS [*m/e*: 242 (M^+)], and the presence of a broad band due to a hydroxyl group at 2200—3400 cm^{-1} (similar to that of 3-pyridinol[4]) and the absence of the carbonyl band at 1715 cm^{-1} were noted in the IR spectrum. The ^{1}H-NMR spectrum is full agreement with the proposed structure. Treatment of IVa with benzoyl chloride and triethylamine in boiling acetone afforded the corresponding *O*-benzoate as colorless needles, mp 140—142°C, in 77% yield; conversely the *O*-benzoate was easily hydrolyzed by 10% sodium hydroxide solution to IVa.

In the previous studies on the reaction of 2,3-lutidine *N*-oxide with IIa,[3] it was proved

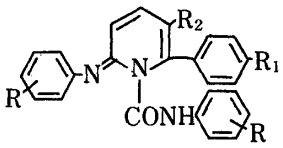
Table I. Yields of Cycloadducts in the Cycloadditions of Substituted Phenyl Isocyanates (II) to 2-Phenylpyridine *N*-Oxides (V—VIII)



cycloadduct (IX—XI)



anilino-type (XII—XIV)



imino-type (XV)

Starting materials					Conditions		Product yields (%)[a]		
IIa—g	Pyridine *N*-oxides	R_1	R_2	R	Reaction temp. (°C)	Reaction time (h)	Cycloadduct (IX—XI)	Anilino (XII—XIV)	Imino (XV)
a	V	H	H	H	70	7	55	Trace	—
a	V	H	H	H	110	5	62	Trace	—
a	V	H	H	H	110	7	70	Trace	—
a	V	H	H	H	110	10	51	12	—
a	V	H	H	H	110	15	10	20	—
a	V	H	H	H	150	7	—	67	—
b	V	H	H	*o*-CH_3	110	7	—	—	—
c	V	H	H	*m*-CH_3	110	7	47	Trace	—
d	V	H	H	*p*-CH_3	110	7	55	—	—
e	V	H	H	*o*-Cl	110	7	—	—	—
f	V	H	H	*m*-Cl	110	7	10	37	—
g	V	H	H	*p*-Cl	110	7	53	22	—
a	VI	H	CH_3	H	70	7	40	—	—
a	VI	H	CH_3	H	110	5	80	—	—
a	VI	H	CH_3	H	110	7	82	—	—
a	VI	H	CH_3	H	110	15	81	—	—
a	VI	H	CH_3	H	150	7	18	65	—
b	VI	H	CH_3	*o*-CH_3	110	7	35	—	—
c	VI	H	CH_3	*m*-CH_3	110	7	71	—	—
d	VI	H	CH_3	*p*-CH_3	110	7	75	—	—
e	VI	H	CH_3	*o*-Cl	110	7	33	—	—
f	VI	H	CH_3	*m*-Cl	110	7	75	—	—
g	VI	H	CH_3	*p*-Cl	110	7	82	—	—
a	VII	CH_3	H	H	110	7	58	—	—
a	VII	NO_2	H	H	110	7	—	30	29

a) Calcd on the basis of 2-phenylpyridine *N*-oxides (V—VIII).

Table II. Analytical Data for Cycloadducts (IX—XI)

Compd. No.	mp (°C)	Appearance (Recryst. solvent)	Formula	Analysis (%) Calcd (Found) C	H	N
IXa	142—143	Colorless needles (*n*-Hexane–benzene)	$C_{18}H_{14}N_2O_2$	74.47 (74.43	4.86 4.87	9.65 9.44)
IXc	103—103	Colorless plates (*n*-Hexane–Me_2CO)	$C_{19}H_{16}N_2O_2$	74.98 (75.18	5.30 5.26	9.21 9.23)
IXd	160—161	Colorless prisms (*n*-Hexane–Me_2CO)	$C_{19}H_{16}N_2O_2$	74.98 (75.23	5.30 5.31	9.21 9.29)
IXf	134—135.5	Colorless prisms (*n*-Hexane–Me_2CO)	$C_{18}H_{13}ClN_2O_2$	66.57 (66.73	4.03 4.13	8.63 8.69)
IXg	189—190	Colorless needles (*n*-Hexane–benzene)	$C_{18}H_{13}ClN_2O_2$	66.57 (66.75	4.03 4.17	8.63 8.40)
Xa	173—174	Colorless needles (*n*-Hexane–Me_2CO)	$C_{19}H_{16}N_2O_2$	74.98 (74.89	5.30 5.07	9.21 9.29)
Xb	156—157	Colorless plates (*n*-Hexane–Me_2CO)	$C_{20}H_{18}N_2O_2$	75.45 (75.44	5.70 5.68	8.80 8.85)
Xc	129—131	Colorless needles (*n*-Hexane–Me_2CO)	$C_{20}H_{18}N_2O_2$	75.45 (75.56	5.70 5.68	8.80 8.85)
Xd	173—174	Colorless needles (*n*-Hexane–Me_2CO)	$C_{20}H_{18}N_2O_2$	75.45 (75.48	5.70 5.61	8.80 8.64)
Xe	180—181	Colorless plates (*n*-Hexane–Me_2CO)	$C_{19}H_{15}ClN_2O_2$	67.36 (67.57	4.46 4.42	8.27 8.32)
Xf	131—132	Colorless needles (*n*-Hexane–Me_2CO)	$C_{19}H_{15}ClN_2O_2$	67.36 (67.09	4.46 4.30	8.27 8.21)
Xg	189—190	Colorless needles (*n*-Hexane–Me_2CO)	$C_{19}H_{15}ClN_2O_2$	67.36 (67.39	4.46 4.56	8.27 8.49)
XIa	139—140	Colorless needles (*n*-Hexane–benzene)	$C_{19}H_{16}N_2O_2$	74.98 (74.87	5.30 5.31	9.21 9.29)

Table III. Spectral Data for Cycloadducts (IX—XI)

Compd. No.	IR (KBr) cm^{-1} (CO)	NMR (in $CDCl_3$, 60 MHz) C_{7a}-H (1H, d-d, $J_{3a,7a}$=9.0 Hz, $J_{7,7a}$=6.0 Hz)	C_{3a}-H (1H, d, $J_{7a,7a}$=9.0 Hz)	C_7-H (1H, d, $J_{7,7a}$=6.0 Hz)	MS (*m/e*) M^+	M^+-CO_2
IXa	1741	5.00	4.00	3.66—1.90	290	246
IXc	1740	4.98	4.01	(12H, m) 3.70—2.00 (11H, m)	304	260
IXd	1740	4.96	4.00	3.66—2.00 (11H, m)	304	260
IXf	1740	4.85	3.86	3.52—1.85 (11H, m)	324, 326	280, 282[a]
IXg	1739	4.73	3.64	3.40—1.70 (11H, m)	324, 326	280, 282[a]
Xa	1764	5.01	4.12	3.80	304	260
Xb	1740	4.85	4.25	3.75	318	274
Xc	1748	5.03	4.15	3.82	318	274
Xd	1750	5.02	4.17	3.82	318	274
Xe	1760	4.78	4.11	3.76	338, 340	294, 296[a]
Xf	1760	5.03	4.15	3.80	338, 340	294, 296[a]
Xg	1730	4.98	4.13	3.78	338, 340	294, 296[a]
XIa	1750	4.97	3.98	3.67—1.80 (11H, m)	304	260

a) Relative intensity 3:1, due to chlorine atom.

TABLE IV. Analytical Data for 6-Anilino-2-phenylpyridines (XII—XIV)

Compd. No.	mp (°C)	Appearance (Recryst. solvent)	Formula	Analysis (%) Calcd (Found) C	H	N	NMR (in $CDCl_3$, 60MHz) τC_5-H (1H, d, $J_{4,5}$= 8.0 Hz)	IR (KBr) cm^{-1} (NH)	MS (*m/e*) M^+
XIIa	104—105	Colorless prisms (Et_2O)	$C_{17}H_{14}N_2$	82.90 (82.97	5.73 5.79	11.37 11.49)	3.26	3175	246
XIIf	54—55	Colorless plates (Et_2O)	$C_{17}H_{13}N_2Cl$	72.73 (72.21	4.67 4.39	9.98 9.75)	3.35	3175	280, 282[a]
XIIg	115—117	Colorless plates (Et_2O)	$C_{17}H_{13}N_2Cl$	72.73 (72.16	4.67 4.78	9.98 9.86)	3.33	3200	280, 282[a]
XIIIa	94—95	Colorless prisms (Et_2O)	$C_{18}H_{16}N_2$	83.04 (82.91	6.20 6.14	10.76 10.71)	3.23	3180	260
XIVa	165—166	Orange needles (Benzene)	$C_{17}H_{13}N_3O_2$	70.09 (70.01	4.50 4.52	14.43 14.42)	2.07—3.30 (m)	3265	291

a) Relative intensity 3: 1, due to chlorine atom.

that the cycloaddition to the 6 position on the pyridine nucleus took place *via* the initial formation of a 1,6-dihydropyridine-form intermediate. In view of this result, we attempted the cycloaddition of 2-phenylpyridine *N*-oxides (V, VII and VIII) and 3-methyl-2-phenylpyridine *N*-oxide (VI).[5] The 1: 1 cycloadducts with II characteristic of 2,3-dihydro-2-oxooxazolo-[4,5-*b*]pyridine were successfully isolated as shown in Table I, and their structures were assigned in the same manner as before.[2] The cycloaddition did not occur when a solution of 2-phenylpyridine *N*-oxide (V) and IIa in dimethylformamide (DMF) was kept below 70°C. On the other hand, heating the same solution at 110°C for seven hours afforded a 1: 1 cycloadduct (IXa) in 70% yield. Its structural assignment is based on the satisfactory elemental analysis [$C_{18}H_{14}N_2O_2$], the MS [*m/e*: 290 (M^+), 246 (M^+-CO_2)], the IR spectrum [1741 cm^{-1} (C=O)] and the ^{1}H-NMR spectrum [τ ($CDCl_3$): 5.00 (1H, dd, $J_{3a,7a}$=9.0, $J_{7,7a}$=6.0 Hz, C_{7a}–H), 4.00 (1H, d, $J_{3a,7a}$= 9.0 Hz, C_{3a}–H), 1.90—3.66 (12H, m, C_6–H, C_7–H, phenyl protons)]. The cycloadduct (IXa) is fairly stable but can be readily transformed into 2-anilino-6-phenylpyridine (XIIa) by heating in DMF at 150°C. Under reflux in ethanolic potassium hydroxide, IXa was also converted to XIIa in good yield. The structure of XIIa was confirmed by the elemental analysis [$C_{17}H_{14}N_2$], the MS [*m/e*: 246 (M^+)], the IR spectrum [3175 cm^{-1} (N–H); the absence of the carbonyl band at 1741 cm^{-1}] and the ^{1}H-NMR spectrum [τ ($CDCl_3$): 3.26 (1H, d, $J_{4,5}$=8.0 Hz, C_5–H)].

The cycloaddition of *o*-substituted phenyl isocyanates (IIb and IIe) to 2-phenylpyridine *N*-oxide (V) failed to give the expected 1: 1 adduct, and that to 3-methyl-2-phenylpyridine *N*-oxide (VI) gave yields of the 1: 1 adducts of less than 35%, although the ability of VI to undergo the cycloaddition should be high. The isocyanato group seems to be more sterically hindered as a result of the restriction imposed on the interaction with the adjacent substituent. 2-(*p*-Nitrophenyl)pyridine *N*-oxide (VIII) bearing an electron-attracting function, in contrast to VII, had a tendency to labilize the cycloadduct, which resulted in increased yields of XIVa and XVa. The ^{1}H-NMR spectrum of XVa in deuterated chloroform exhibited one proton signal due to the olefinic hydrogen on the beta carbon as a doublet ($J_{4,5}$=8.3 Hz) at τ 3.53, similar to that of 1,2-dihydro-1-phenylcarbamoyl-2-phenyliminopyridine.[1,6] The MS and elemental analysis were consistent with empirical formula for the carbamation product of XIVa.

Experimental

All melting points are uncorrected. IR spectra were recorded on a Nippon Bunko DS-301 infrared spectrophotometer. ^{1}H-NMR spectra were taken with JNM-MH-100 and JNM-C-60H spectrometers in

ca. 5% (w/v) solution with tetramethylsilane as an internal standard, and chemical shifts are expressed as τ values. MS were taken with a JEOL JMS-01SG spectrometer.

Reaction of 2,3-Lutidine *N*-Oxide (I) with Phenyl Isocyanate (IIa)——Phenyl isocyanate (4.85 g, 0.04 mol) was added dropwise to a solution of 2.50 g (0.02 mol) of I in 16.4 ml of DMF at room temperature with stirring and the reaction mixture was heated at 110°C for 7 h. After cooling, the reaction mixture was concentrated *in vacuo* below 70°C and then 20 ml of Et_2O was added to the residue. The mixture was left overnight at 0—5°C, and the precipitated crystals were collected by suction, washed with a small amount of Et_2O and recrystallized from Me_2CO to give 2,3,3a,4,5,7a-hexahydro-6-methyl-2-oxo-3-phenyl-5-(*N*-phenylcarbamoyl)methylene-oxazolo[4,5-*b*]pyridine (IIIa) as colorless prisms, mp 227—229°C, in 21% yield. IR ν_{max}^{KBr} cm^{-1}: 3300 (–NH–), 1715 and 1660 (C=O). ^{1}H-NMR (DMSO-d_6) at 100 MHz: τ 8.05 (3H, narrow d, CH_3), 4.80 (1H, s, =CH–), 4.54—4.72 (1H, m, C_{7a}-H), 3.85—4.20 (2H, m, C_7– and C_{3a}–H), 2.40—3.30 (10H, m, two phenyl protons), 0.63 (1H, d, $J_{3a,4}$=3 Hz, C_4–H, exchangeable with D_2O), 0.42 (1H, br s, –CONH–). MS: *m/e*: 361 (M^+), 317 (M^+-CO_2), 269 (M^+—NH—Ph), 241 (M^+—CONH—Ph). *Anal.* Calcd for $C_{21}H_{19}N_3O_3$: C, 69.79; H, 5.30; N, 11.63. Found: C, 69.81; H, 5.38; N, 11.68.

Hydrolysis of IIIa——A mixture of 1.0 g of IIIa and 10 ml of 2.5% KOH–EtOH was refluxed for 1 h. The solvent was removed *in vacuo* and then 10 ml of H_2O was added to the residue. The alkaline solution was neutralized with 10% HCl. The precipitated crystals were collected by suction and recrystallized from Me_2CO to give IVa as colorless needles, mp 245—246°C, in 95% yield. IR ν_{max}^{KBr} cm^{-1}: 3225 (–NH–), 2200—3400 (OH), 1665 (C=O). ^{1}H-NMR (DMSO-d_6) at 100 MHz: τ 7.78 (3H, s, CH_3), 6.28 (2H, s, $-CH_2-$), 2.38—3.20 (6H, m, C_4–H and phenyl protons), 2.24 (1H, d, $J_{4,6}$=2.6 Hz, C_6–H), 0.50 (1H, br s, –CONH–), 0.05 (1H, br s, OH).[7] MS: *m/e*: 242 (M^+). *Anal.* Calcd for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.83; N, 11.56. Found: C, 69.54; H, 5.72; N, 11.59.

Benzoylation of IVa——Benzoyl chloride (320 mg, 0.0025 mol) was added dropwise to a solution of 500 mg (0.002 mol) of IVa and 5 ml of Et_3N in 70 ml of Me_2CO, and the mixture was refluxed for 1 h. After cooling, $Et_3N\cdot HCl$ precipitated and was filtered off. The filtrate was concentrated *in vacuo* and triturated with 30 ml of Et_2O to give a crystalline mass, which was filtered off, washed with H_2O and recrystallized from Me_2CO, giving 550 mg (77%) of the *O*-benzoate of IVa as colorless needles, mp 140—142°C. IR ν_{max}^{KBr} cm^{-1}: 3300 (–NH–), 1720 and 1645 (C=O). ^{1}H-NMR ($CDCl_3$) at 60 MHz: τ 7.58 (3H, s, CH_3), 6.12 (2H, s, $-CH_2-$), 1.74—3.05 (11H, m, pyridine C_4–H and two phenyl protons), 1.66 (1H, d, $J_{4,6}$=2.6 Hz, pyridine C_6–H), 0.67 (1H, br s, –CONH–). MS: *m/e*: 346 (M^+). *Anal.* Calcd for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.82; H, 5.12; N, 8.03. Hydrolysis of the *O*-benzoate with hot 10% NaOH aq. soln. for a short period gave IVa in 90% yield.

Reaction of 2-Phenylpyridine *N*-Oxides (V—VII) with II——As a typical run, 1.2 g (0.01 mol) of IIa was added dropwise to a solution of 0.93 g (0.005 mol) of VI in 4.3 ml of DMF at room temperature with stirring, and the mixture was heated in an oil bath. After the time indicated in Table I, the reaction mixture was concentrated *in vacuo* below 70°C and the residue was dissolved in Et_2O. The solution was allowed to stand overnight at 0—5°C and the precipitated crystals were collected by suction, washed with a small amount of Et_2O and recrystallized from hexane–Me_2CO to give the cycloadduct (Xa) (Tables II and III). After removal of Xa, the viscous filtrate was dissolved in a small amount of $CHCl_3$ and chromatographed over 40 g of silica gel (200 mesh), $CHCl_3$ being used as an eluent. The crude anilinopyridine (XIIIa) was obtained from the first effluent fraction and recrystallized from Et_2O (Tables I and IV).

Hydrolysis of Xa——A solution of 1.0 g of Xa in 10% KOH–EtOH (10 ml) was refluxed for 30 min, then the solvent was removed *in vacuo*. The residue was extracted with Et_2O. Removal of the solvent left a residue which was recrystallized from Et_2O to give colorless prisms (XIIIa), mp 94—95°C, in 95% yield (0.81 g) (Table IV).

Reaction of 2-(*p*-Nitrophenyl)pyridine *N*-Oxide (VIII) with IIa——Phenyl isocyanate (1.10 g) was added dropwise to a solution of 1.0 g of VIII in 5 ml of DMF and the mixture was heated at 110°C for 7 h. After cooling, the reaction mixture was concentrated *in vacuo* below 70°C and the residue was dissolved in Et_2O. The solution was left overnight at 0—5°C, and the precipitated crystals were collected by suction. The crystals were dissolved in a small amount of $CHCl_3$ and chromatographed over 40 g of silica gel (200 mesh), $CHCl_3$–benzene (4: 6) being used as an eluent. A crystalline mass was obtained from the first effluent fraction and recrystallized from benzene to give light yellow prisms (XVa), mp 176—177°C, in 29% yield (0.55 g). IR ν_{max}^{KBr} cm^{-1}: 3000—3250 (N–H), 1675 (C=O). ^{1}H-NMR ($CDCl_3$) at 60 MHz: τ 3.53 (1H, d, $J_{4,5}$=8.3 Hz, C_5–H), 2.17—3.23 (12H, m, C_3–H, C_4–H, two phenyl protons), 1.97 (2H) and 1.67 (2H) (A_2B_2 pattern of 4′-nitro-1′-phenyl part, J=9.0 Hz), −2.28 (1H, s, N–H). MS: *m/e*: 410 (M^+), 290 (M^+—CONH—Ph). *Anal.* Calcd for $C_{24}H_{18}N_4O_3$: C, 70.23; H, 4.42; N, 13.65. Found: C, 70.21; H, 4.25; N, 13.71. After removal of XVa, the viscous filtrate was dissolved in a small amount of $CHCl_3$ and chromatographed over silica gel in the same manner as mentioned before. A crystalline mass was obtained from the first effluent fraction and recrystallized from benzene to give orange needles (XIVa), mp 165—166°C, in 30% yield (0.40 g) (Table IV).

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