spectrometry. Elemental analyses were performed by the members of Department of Pharmaceutical Sciences, University of Tokyo, and Kowa Pharmaceutical Co. Ltd., to whom he is also thankful.

Summary

Reactivity of 3,6-dichloropyridazine 1-oxide (II) to nucleophilic substitution was examined. 3-Chlorine atom was always more reactive than 6-chlorine atom. Chlorine of 3-substituted-6-chloropyridazine 1-oxide was more reactive than that of 3-substituted-6-chloropyridazine.

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154. Masatomo Hamana, Bunsuke Umezawa, and Shoichi Nakasima : Studies on Tertiary Amine Oxides. XIII. Reactions of N-(*p*-Dimethylaminophenyl)nitrones having Pyridine N-Oxide, Quinoline or its N-Oxide as α-Substituent.

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Previously, it[1] was reported that N-(*p*-dimethylaminophenyl)-α-(1-oxido-2-pyridyl)-nitrone (PO-2) underwent a facile rearrangement to the corresponding acid anilide in the presence of several reagents, among which sulfur dioxide was most specific, and that the presence of both N-(*p*-dimethylaminophenyl) and α-(1-oxido-2-pyidyl) group in (PO-2) was shown to be favorable for the rearrangement. In order to examine the effect of heteroaromatic rings (quinoline or pyridine), ring position bearing the substituent of α-(N-dimethylaminophenylnitrone) group (2- or 4-position), and N-oxidation of the rings, syntheses of five nitrones, N-(*p*-dimethylaminophenyl)-α-(1-oxido-4-pyridyl) (PO-4), N-(*p*-dimethylaminophenyl)-α-(2-quinolyl) (Q), N-(*p*-dimethylamiophenyl)-α-(1-oxido-2-quinolyl) (QO), N-(*p*-dimetylaminophenyl)-2-(4-quinolyl) (L) and N-(*p*-dimethylaminophenyl)-α-(1-oxido-4-quinolyl)nitrone (LO) were carried out and they were subjected to the reaction with six sorts of reagent namely, sulfur dioxide, triphenyl phosphite, phosphorus trichloride, phosphoryl chloride and acetic anhydride. All nitrones used were prepared easily from the corresponding pyridinium salts by the King reaction, except (PO-4), which was obtained by the same route as employed in the synthesis of an authentic specimen of (PO-2)[2] as shown in Chart 1.

The fact that 4-picoline 1-oxide could not be converted to the corresponding pyridinium salt by King's method appeared to show -I effect of N-oxide group diminishing greatly at 4-position, which located remote for from the functional group than 2-position by two carbon atoms in pyridine ring.

Corresponding anils and acid anilides, expected as reaction products, were synthesized by the following unequivocal route.

Specificities, hitherto known, of the above reagents could be summarized as below. Sulfur dioxide was a deoxygenative reagent for aliphatic tertiary amine N-oxide[3] or

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*1 Katakasu, Fukuoka (浜名政和, 梅沢文輔, 中島松一).

1) B. Umezawa : This Bulletin, 8, 698 (1960).
2) M. Hamana, B. Umezawa, Y. Gotoh, K. Noda : *Ibid.*, 8, 692 (1960).
3) E. Ochiai : J. Org. Chem., 18, 534 (1953).

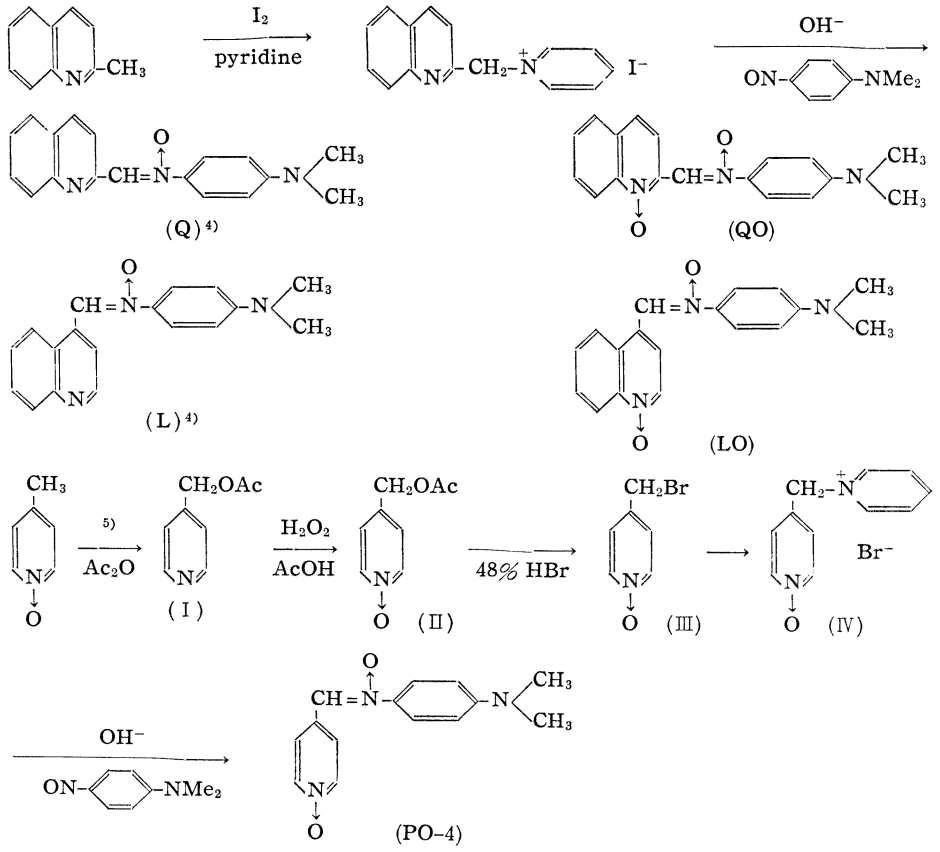


Chart 1. Syntheses of Nitrones

nitrones, and some of the latter could undergo rearrangent.[6] Phosphorus trichloride[7] or triphenyl phosphite[8] was used for deoxygenation of aromatic tertiary amine N-oxide or nitrones, which could be rearranged by phosphoryl chloride or acetic anhydride, the latter of which was known to cause rearrangement of aromatic tertiary amine N-oxides. Triphenyl phosphate, though not so effective as phosphoryl chloride, may be applicable as a rearrangement reagent to some nitrones.

Apparent complexity of the results (Table I) appeared to be due to the side reaction; i.e. anils formed in the case of phosphoryl chloride or triphenyl phosphate would have been given through the hydrolysis of the starting nitrones followed by the recombination of aldehydes and N,N-dimethyl-*p*-phenylenediamine, one of the disproportionation products of N-(*p*-dimethylaminophenyl)hydroxylamine, as reported before.[6] The results of main reaction, deoxygenation and rearragement, were shown in Table II. Examination of the results obtained above revealed that three generalizations could be made as shown in Table III.

4) L.C. King, S.V. Abramo : J. Org. Chem., **23**, 1609 (1958).
5) J.A. Berson, T. Cohen : J. Am. Chem. Soc., **77**, 1281 (1955); V. Boekelheide, W.J. Linn : *Ibid.*, **76**, 1286 (1954); O.H. Bulitt, J.T. Maynard : *Ibid.*, **76**, 1370 (1954).
6) B. Umezawa : This Bulletin, 8, 967 (1960).
7) M. Hamana : Yakugaku Zasshi, **71**, 263 (1953).
8) *Idem* : *Ibid.*, **75**, 139 (1955).

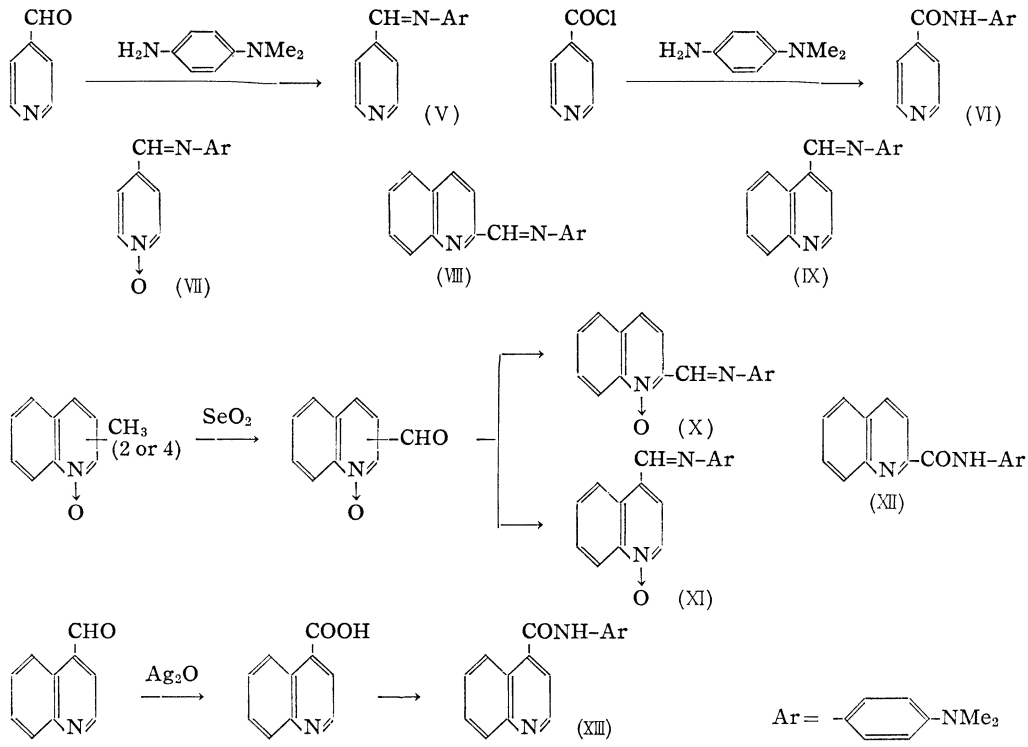


Chart 2. Shntheses of Anils and Acid Anilides

Table I. Reaction Conditions and Products

	SO_2	$P(OPh)_3$	$PO(OPh)_3$	PCl_3	$POCl_3$	Ac_2O
(PO-2)		no change (23.3)	no change (40)			
	anilide (50)	anilide (trace)	anilide (20)	anilide[a] (82)	anilide[a,b] (4.6) anilide (13.8)	anilide (30)
(PO-4)		no change (50)				no change (24)
	anilide (30)	anilide (6.6)	anilide (80)	anilide[a] (28.3)	anilide[a,c] (29) anilide (6)	anilide (24)
(Q)	anil (31.7)	anil (35.3)	no change (36.7)	anilide (34)	anilide (23.3)	anilide (56.5)
(L)		no change (3.3)	no change (53.4)			
	anil (21.2)	anil (14.3)	anil (10)	anil (2)	anil[c] (28.4)	
	anilide (4)	anilide (trace)	anilide (trace)	anilide (22)	anilide (24)	anilide (50)
(QO)		no change (26.6)				
	anil (52.4)	anil (3.7)	no change (83.5)	anilide[a] (56.3)	anilide (13.3)	anilide (24.3)
(LO)		no change (22)				
	anil (1.5)	anil (6.3)	anil (trace)			
	anilide (33.4)	anilide (trace)	anilide (74)	anilide[a] (27.4)	anilide[a] (1.5)	anilide (53)
Condition	ice-cooling, 2 hr. in $CHCl_3$	reflux, 3 hr. in $CHCl_3$	reflux, 2 hr. in $CHCl_3$	reflux, 1 hr. in $CHCl_3$	room temp., 3 hr.	room temp., 6 hr.

Yield is shown in parentheses in per cent. The corresponding deoxygenated or rearranged product is given as anil or anilide.

a) a deoxygenated product of aromatic N-oxide. *b*) reflux, 2 hr. *c*) room temp., overnight.

No consideration on reactions with Ac_2O was made in this paper lbecause of obscurity of the reaction mechanism : cf. F. Kröhnke : Ann., **604**, 203 (1957); E. Schmitz : Chem. Ber., **91**, 1488 (1958).

Table II.

Reagent / Nitrone	SO_2	$P(OPh)_3$	$PO(OPh)_2$	PCl_3	$POCl_3$	Ac_2O
(PO-2)		N	N			
	R	Δr	r	R	R	R
(PO-4)		N				n
	R	r	R	R	R	r
(Q)	A	A	N	R	R	R
(L)		A	N			
	A	n	a	R	a	
	r	Δr	Δr	a	r	R
(QO)		N				
	A	a	N	R	R	R
(LO)		N				
	R	Δr	R			
	a	a	Δa	R	R	R

N : starting nitrone (major) A : anil (major) R : rearrangement (major)
n : starting nitrone (minor) a : anil (minor) r : rearrangement (minor)
Δa : anil (trace) Δr : rearrangement (trace)

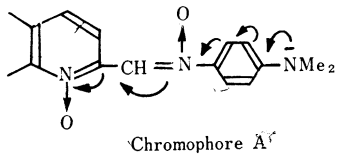
Table III.

	Rearrangement	Deoxygenation
1. 2- and 4-Series	2<4	2>4
2. Quinoline and pyridine series	quinoline < Pyridine	quinoline > Pyridine
3. Aromatie tertiary amine and its N-oxide	$\overset{\diagup}{\overset{\diagdown}{N}} < \overset{\diagup}{\overset{\diagdown}{N}}\rightarrow O$	$\overset{\diagup}{\overset{\diagdown}{N}} > \overset{\diagup}{\overset{\diagdown}{N}}\rightarrow O$

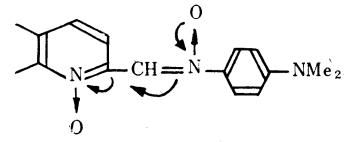
1) The 4-series was more favorable than the 2-series in rearrangement and *vice versa* in deoxygnation, e. g. with sulfur dioxide or triphenyl phosphite. (OQ) was more easily deoxygenated than (LO), while the latter was more susceptible to the rearrangement than the former. 2) In regard to nitrones with quinoline or pyridine ring (the substituted position of nitrone group was the same), deoxygenation with sulfur dioxide occurred more easily in the former than the latter. Conversely, the former was more difficult to undergo rearrangement with the reagent. 3) By N-oxidation of heteroaromatic ring, nitrones did not tend to undergo facile deoxygenation but rearrangement as seen in the reaction of (L) or (LO) with sulfur dioxide or triphenyl phosphate.

On the basis of cross conjugation*2 in these nitrones and of -I effect of the nitrogen atom in heteroaromatic ring, the results shown in 1) or 2) seemed to be well interpreted. Namely, the deoxygenation and the rearrangement in these nitrones would be a kind of competitive reaction and the -I effect would be more dominant at 2- rather than 4-position in heteroaromatic ring (see above) and that of quinoline would be stronger than that of pyridine ring (see ultra violet spectral data).

Therefore, if chromophore A were predominant over chromophore B owing to the —I effect of heteroaromatic ring, the N-O bond of nitrone might well be present as a



Chromophore A



Chromophore B

Chart 3.

*2 One conjugation including *p*-dimethylaminophenyl group and aromatic ring (Chromophore A) and the other nitrone grouping and the latter (Chromophore B).

co-ordinate single bond and deoxygenated readily rather than rearranged. However, the effect of N-oxide, as shown in 3), seemed to be contray to what anticipated from the −I effect only. This discrepancy would be due to +M effect of N-oxide and the group would participate in the rearrangement in such a way as shown in Chart 4. At first, −I effect of N-oxide group would favor the formation of a cyclic intermediate as mentioned before,[1] and the next stage of hydrid shift from carbon to nitrogen atom would be accelerated by +M effect of the same group to complete the rearrangement.

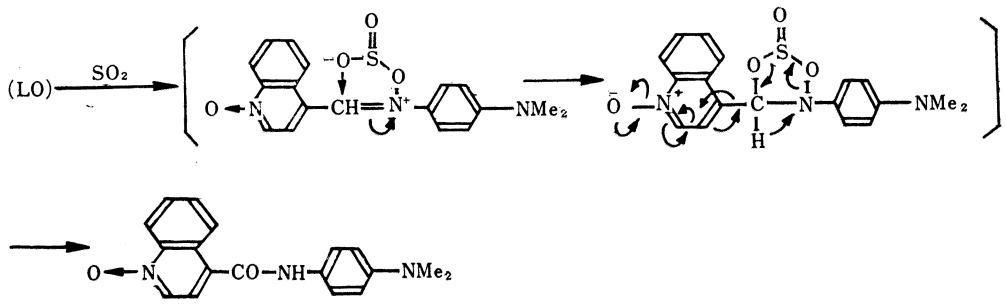
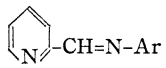
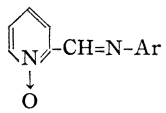


Chart 3. Participation of N-Oxide Group in the Rearrangement

The result that the +M effect in quinoline series was marked only at 4-position seemed to be proportional to the fact that quinoline 1-oxide was nitrated almost exclusively in the position. In this connection, ultraviolet spectra of these nitrones together with their corresponding anils were taken in a hope of obtaining some support for the above discussion (Table IV). However, the variance of absorption band caused by cross conjugation was so complicated that only the following characteristics about K bands could be clarified : 1) N-Oxidation of heteroaromatic ring caused a bathochromic and hyperchromic displacement. 2) Nitrones or anils with quinoline ring had absorption at

Table IV. UV Spectra of Nitrones and Anils

	λ_{max} mμ (ε_{max})			
				K Bands
		250 (14,240)		400 (10,400)
		248 (21,100)		440 (20,400)
(PO-2)	241 (12,120)	262 (12,740)	324 (11,340)	426 (17,800)
(V)		250 (15,500)		408 (11,300)
(VII)	230 (11,600)	255 (10,400)	306 (13,500)	442 (16,200)
(PO-4)	240 (14,150)	342 (16,200)		420 (21,800)
(VIII)	230 (29,000)	250 (29,200)	294 (11,250)	415 (15,700)
(X)	232 (23,500)	268 (21,450)	312 (11,500)	472 (22,050)
(Q)	222 (24,500)	290 (12,200)	325 (13,950)	410 (21,300)
(QO)	236 (25,750)	310 (20,250)	370 (11,700)	455 (21,800)
(IX)	230 (19,600)	246 (21,600)	315 (7,500)	432 (14,550)
(XI)	244 (29,200)	365 (9,800)		470 (17,500)
(L)	248 (18,000)	340 (12,250)		420 (19,600)
(LO)	252 (23,000)	390 (14,500)		448 (23,500)

Ultraviolet spectra were measured in 95% EtOH (concentration : $2\times10^{-4}M$) with a Beckman DK 2 spectrophotometer.
Dilution of all nitrones was carried out in dark place.

longer wave length in higher intensity than those with pyridine ring. 3) On conversion of azomethin group to aldonitrone (formation of cross conjugation), hypsochromic shift was observed without any apparent change in wave length.

Experimental

All melting points were uncorrected and all reaction products were identified by mixed fusion with authentic specimens. Chromatographies were carried out over alumina (elution with $CHCl_3$). An example of full procedure was shown on the synthesis of pyridinium salts, nitrones, aldehydes, anils or anilides respectively.

Syntheses of Nitrones

N-(*p*-Dimethylaminophenyl)-α-(1-oxido-4-pyridyl)nitrone (PO-4) 4-Pyridinemethanol Acetate (I)——To 400 cc. of Ac_2O (60~65°), a solution of 100 g. of γ-picoline 1-oxide in $CHCl_3$ was added dropwise. The mixture was maintained at the same temperature for 2.5 hr. and an excess of Ac_2O was distilled off to give (I), $b.p_6$ 80~100°, yield, 74 g.

4-Pyridinemethanol Acetate 1-Oxide (II)——A mixture of 74 g. of (I), 370 cc. of AcOH and 84 cc. of 30% H_2O_2 was kept at 70~80° for 12 hr. After an excess of H_2O_2 and AcOH was distilled off, the base was taken up in $CHCl_3$. Usual treatment of the $CHCl_3$ layer gave (II), $b.p_5$ 160~175°, yield, 22 g.

4-Bromomethylpyridine 1-Oxide Hydrobromide (III)——A solution of 20 g. of (II) in 150 cc. of 48% HBr was refluxed for 4 hr. in an oil bath. After distilling off the solvent, the residue was crystallized from EtOH to give (III), m.p. 161~162°, 21 g. (69% yield).

1-(1-Oxido-4-pyridylmethyl)pyridinium Bromide (IV)——A solution of 21 g. of (III) in water was made alkaline with K_2CO_3 under ice-cooling. The base was extracted with $CHCl_3$, to which 10 g. of pyridine was added and the mixture was maintained overnight in a refrigerator. After distilling off $CHCl_3$, recrystallization from a mixture of abs. EtOH and AcOEt quantitatively afforded (IV), m.p. 56~57°, yielding 22 g., monopicrate, m.p. 209~210°. *Anal.* Calcd. for $C_{17}H_{14}O_8N_5$: C, 49.04; H, 3.36; N, 16.77. Found: C, 49.29; H, 3.37; N, 16.43.

(PO-4)——To a solution of 22 g. of (IV) in water, EtOH solution of *p*-nitroso-N,N-dimethylaniline was added and a solution of 5.3 g. of KOH in 10 cc. of water was added dropwise under stirring with ice-cooling. The mixture was diluted with water and the crystals precipitated were collected and recrystallized from AcOEt to give (PO-4), m.p. 217~218° (decomp.), 9 g. (42.5% yield). *Anal.* Calcd. for $C_{14}H_{15}O_2N_3 \cdot H_2O$: C, 61.08; H, 6.22; N, 15.62. Found: C, 61.53; H, 6.13; N, 15.11.

N-(*p*-Dimethylaminophenyl)-α-(4-quinolyl)nitrone (L)——M.p. 195~196° (EtOH). *Anal.* Calcd. for $C_{18}H_{17}ON_3$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.02; H, 5.92; N, 14.44.

N-(*p*-Dimethylaminophenyl)-α-(1-oxido-2-quinolyl)nitrone (QO)——Reddish leaves, m.p. 207~208° (decomp.) (MeOH). 78.5% yield. *Anal.* Calcd. for $C_{18}H_{17}ON_3$: C, 70.34; H, 5.58; N, 13.67. Found: C, 70.61; H, 5.75; N, 13.32.

N-(*p*-Dimethylaminophenyl)-α-(1-oxido-4-quinolyl)nitrone (LO)——M.p. 218~219° (EtOH). 38.6% yield. *Anal.* Calcd. for $C_{18}H_{17}ON_3$: C, 70.34; H, 5.58; N, 13.67. Found: C, 70.09; H, 5.73; N, 13.69.

Syntheses of Aldehydes

Quinaldaldehyde 1-Oxide——To a solution of 3.3 g. of SeO_2 in 30 cc. of dioxane (70~80°), a solution of 4 g. of quinaldine 1-oxide in 4 cc. of dioxane was added dropwise. The mixture was refluxed for 1 hr. to deposit Se, which was filtered off. An addition of MeOH to the concentrated filtrate gave crystals which were discarded. Chromatography of the residue afforded quinoline-2-aldehyde 1-oxide, m.p. 95~96° (from a mixture of benzene and petr. benzin), yellow needles. Oxime, yellow leaves, m.p. 215~217° (MeOH). *Anal.* Calcd. for $C_{18}H_8O_2N$: C, 63.82; H, 4.29; N, 14.89. Found: C, 63.58; H, 4.24; N, 14.50.

Cinchoninaldehyde 1-Oxide——M.p. 160° (from a mixture of benzene and petr. ether). *Anal.* Calcd. for $C_{10}H_7O_2N$: C, 69.39; H, 4.07; N, 8.09. Found: C, 69.51; H, 4.23; N, 8.03.

Syntheses of Anils

N,N-Dimethyl-N'-(4-pyridylmethylene)-*p*-phenylenediamine (V)——To a solution of 1 g. of isonicotinaldehyde in EtOH, was added a solution of 1.5 g. of N,N-dimethyl-*p*-phenylenediamine in EtOH. The mixture was allowed to stand overnight at room temperature. Recrystallization from benzene afforded (V), m.p. 191~192°, yellow needles. *Anal.* Calcd. for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.87; H, 6.71; N, 18.98.

4-(*p*-Dimethylaminophenyliminomethyl)pyridine 1-Oxide (VII)——M.p. 207~208° (AcOEt). *Anal.* Calcd. for $C_{14}H_{15}ON_3$: C, 69.69; H, 6.27; N, 17.42.

N,N-Dimethyl-N'-(2-quinolylmethylene)-*p*-phenylenediamine (VIII)——Yellow plates, m.p. 145~146° (MeOH). *Anal.* Calcd. for $C_{18}H_{17}N_3$: C, 78.41; H, 6.22; N, 14.80.

N,N-Dimethyl-N′-(4-quinolylmethylene)-*p*-phenylenediamine (IX)——Reddish leaves, m.p. 155～156°(MeOH). *Anal.* Calcd. for $C_{18}H_{17}N_3$: C, 78.41; H, 6.22; N, 15.26. Found: C, 78.41; H, 6.26; N, 15.05.

2-(*p*-Dimethylaminophenyliminomethyl)quinoline 1-Oxide (X)——Red needles, m.p. 214～215°(benzene). *Anal.* Calcd. for $C_{18}H_{17}CN_3$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.39; H, 5.70; N, 13.96.

4-(*p*-Dimethylaminophenyliminomethyl)quinoline 1-Oxide (XI)——M.p. 178～179°(from a mixture of benzene and petr. ether). *Anal.* Calcd. for $C_{18}H_{17}ON_3$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.38; H, 6.02; N, 14.22.

Syntheses of Pyridinium Salts

1-(1-Oxido-2-quinolylmethyl)pyridinium Iodide (XIV)——To a warm solution (40～50°) of 10 g. of quinaldine 1-oxide in 18 cc. of pyridine, 18.2 g. of I_2 was added gradually. The mixture was heated for additional 2 hr. at 100°. The resulting crystals were washed with Et_2O, water and Me_2CO. Recrystallization from aqueous EtOH gave (XIV), yellow rods, m.p. 195～196°, 8 g. (36.6% yield). *Anal.* Calcd. for $C_{15}H_{13}ON_2$: C, 49.45; H, 3.57; N, 7.69. Found: C, 49.59; H, 3.65; N, 7.99.
Monopicrate: m.p. 214～215°. *Anal.* Calcd. for $C_{21}H_{16}O_8N_5$: C, 54.20; H, 3.25; N, 15.05. Found: C, 54.18; H, 3.21; N, 14.73.

1-(1-Oxido-4-quinolylmethyl)pyridinium Iodide (XV)——M.p. 208～209°(decomp.), 53.5% yield. *Anal.* Calcd. for $C_{15}H_{13}ON_2J\cdot H_2O$: C, 47.20; H, 3.94; N, 7.33. Found: C, 47.57; H, 4.19; N, 6.94.
Monopicrate: m.p. 218～219°(MeOH). *Anal.* Calcd. for $C_{21}H_{16}O_8N_5$: C, 54.20; H, 3.25; N, 15.05. Found: C, 53.76; H, 3.67; N, 14.83.

Syntheses of Anilides

4′-Dimethylaminoisonicotinanilide (VI)——A mixture of 2 g. of isonicotinic acid and 15 g. of $SOCl_2$ was refluxed for 10 min. until a clear solution was obtained. An excess of $SOCl_2$ was distilled off under reduced pressure. The resulting crystals of isonicotinyl chloride hydrochloride was suspended in benzene and to the suspention, a trace of pyridine and 0.9 g. of N,N-dimethyl-*p*-phenylenediamine were added. The mixture was kept in a refrigerator overnight to deposit crystals, recrystallization of which from benzene afforded (VI), faint yellow leaves, m.p. 221～222°. *Anal.* Calcd. for $C_{14}H_{15}ON_3$: C, 69.69; H, 6.27; N, 17.42. Found: C, 69.26; H, 6.48; N, 17.01.

4′-Dimethylaminoquinaldanilide (XII)——Yellow rods (MeOH), m.p. 136～137°. *Anal.* Calcd. for $C_{18}H_{17}ON_3$: C, 74.20; H, 5.88; N, 14.42. Found: C, 73.96; H, 5.92; N, 14.35.

4′-Dimethylaminocinchoninanilide (XIII)——Yellow leaves, m.p. 222～223°(MeOH). *Anal.* Calcd. for $C_{18}H_{17}ON_3$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.18; H, 6.21; N, 14.46.

Reactions of (PO-4)——a) with SO_2: Dried SO_2 was passed through a solution of 300 mg. of (PO-4) in 30 cc. of $CHCl_3$ for 2 hr. under ice-cooling. Washing of the solution with dil. K_2CO_3 and recrystallization of the product afforded 4′-dimethylamino-isonicotinanilide 1-oxide (XVI), 100 mg. (30% yield), m.p. 242～243°. *Anal.* Calcd. for $C_{14}H_{15}O_2N_3$: C, 65.35; H, 5.88; N, 16.33. Found: C, 65.71; H, 5.98; N, 16.38. IR: λ_{max}^{Nujol} 6.10 (amide I), 6.55 μ (amide II). To a solution of 100 mg. of (XVI) in $CHCl_3$, a solution of 70 mg. of PCl_3 in the same solvent was added dropwise under stirring with ice-cooling, and the mixture was refluxed for 1 hr. Recrystallization from MeOH afforded (VI), yellow leaves, m.p. 222～223°, yield 60 mg. b) with PCl_3: To a solution of 300 mg. of (PO-4) in 10 cc. of $CHCl_3$, a solution of 210 mg. of PCl_3 in the same solvent was added dropwise under stirring with ice-cooling. The mixture was refluxed on a water bath for 1 hr. After a usual treatment, recrystallization of the product from MeOH afforded (VI), 60 mg. (28.3% yield). c) with $POCl_3$: To a solution of 500 mg. of (PO-4) in 10 cc. of $CHCl_3$, a solution of 300 mg. of $POCl_3$ in the same solvent was added dropwise under stirring with ice-cooling, and the mixture was allowed to stand overnight at room temperature. After a usual treatment, the product was chromatographied. The first fraction gave (VI), 130 mg. (29% yield). The second fraction afforded (XVI), 30 mg. (6% yieled). d) with $PO(OPh)_3$: To a solution of 100 mg. of (PO-4) in 10 cc. of $CHCl_3$, a solution of 130 mg. of $PO(OPh)_3$ was added and the mixture was refluxed for 2 hr. $CHCl_3$ was evaporated and the residue was recrystallized from MeOH to give (XVI), 80 mg. (80% yield). e) with $P(OPh)_3$: To a solution of 300 mg. of (PO-4) in 10 cc. of $CHCl_3$, a solution of 360 mg. of $P(OPh)_3$ in the same solvent was added and the mixture was refluxed for 3 hr. A usual treatment of the product gave (PO-4), 150 mg. (50% recovery), and (XVI), 20 mg. (6.6% yield). f) with Ac_2O: To a solution of 500 mg. of (PO-4) in 10 cc. of $CHCl_3$, 15 cc. of Ac_2O was added and the mixture was allowed to stand at room temperature for 6 hr. After an excess of Ac_2O and solvent was distilled off, the residue was chromatographed. The first fraction: 4′-dimethylamino-acetoanilide, m.p. 129～130°(from a mixture of benzene and petr. benzin). The second fracton: (PO-4), 120 mg.) 24% recovery). The third fraction: (XVI), 120 mg. (24% yield).

The following reactions were carried out in the same way as in the case of (PO-4). Therefore, the amount of reagents, the product and its yield were described. Reaction conditions were shown only in special cases.

Reactions of (Q)——a) with SO_2: From 500 mg. of (Q), 150 mg. of (VIII), m.p. 143～144°(31.7% yield), was obtained. b) with PCl_3: From 500 mg. of (Q) and 350 mg. of PCl_3, 170 mg. of (XII) (34% yield),

was obtained. c) with $POCl_3$: A mixture of 300 mg. of (Q) and 180 mg. of $POCl_3$ in $CHCl_3$ was allowed to stand at room temperature for 3 hr. After a usual treatment, 70 mg. of (XII) (23.3% yield), was obtained. d) with $PO(OPh)_3$: From 300 mg. of (Q) and 330 mg. of $PO(OPh)_3$, (Q) 110 mg. (36.7% recovery), was recovered. e) with $P(OPh)_3$: From 300 mg. of (Q) and 320 mg. of $P(OPh)_3$, (VIII), 100 mg. (35.3% yield) was obtained. f) with Ac_2O: From 300 mg. of (Q) and 10 cc. of Ac_2O, (XII), 170 mg. (56.5% yield), was obtained.

Reactions of (L)——a) with SO_2: From 500 mg. of (L), (IX), 100 mg. (21.2% yield), and (XIII), 20 mg. (4% yield), were obtained. b) with PCl_3: From 500 mg. of (L) and 350 mg. of PCl_3, (IX), 10 mg. (2% yield) and (XIII), 110 mg. (22% yield), were given. c) with $POCl_3$: From 300 mg. of (L) and 180 mg. of $POCl_3$, (IX), 80 mg. (28.4% yield) and (XIII), 70 mg. (24% yield) were obtained. d) with $PO(OPh)_3$: From 300 mg. of (L) and 330 mg. of $PO(OPh)_3$, (L), 170 mg. (53.4% recovery), (IX), 30 mg. (10% yield) and trace of (XIII) were obtained. e) with $P(OPh)_3$: From 300 mg. of (L) and 320 mg. of $P(OPh)_3$, (L) 10 mg. (3.3% recovery), (IX), 40 mg. (14.3% yield), and trace of (XIII), were obtained. f) with Ac_2O: From 500 mg. of (L) and 15 cc. of Ac_2O, (XIII), 250 mg. (50% yield) was obtained.

Reactions of (QO)——a) with Ac_2O: From 700 mg. of (QO) and 10 cc. of Ac_2O, 4′-dimethylaminoquinaldanilide 1-oxide (XVII), m.p. 222~223°, 170 mg. (24.3% yield), was obtained. IR λ_{max}^{Nujol} μ: 6.0 (amide I), 6.6 (amide II). *Anal.* Calcd. for $C_{18}H_{17}O_2N_3$: C, 70.34; H, 5.58; N, 13.67. Found: C, 70.42; H, 5.63; N, 13.38. (XVII) was deoxygenated with PCl_3 to (XII). b) with SO_2: From 300 mg. of (QO), (X), 150 mg. (52.4% yield) was obtained. c) with PCl_3: From 300 mg. of (QO) and 210 mg. of PCl_3, (XII), 160 mg. (56.3% yield) was given. d) with $POCl_3$: A solution of 300 mg. of (QO) and 180 mg. of $POCl_3$ in $CHCl_3$ was allowed to stand at room temperature for 3 hr. After a usual treatment, (XVII), 40 mg. (13.3% yield) was given. e) with $PO(OPh)_3$: From 300 mg. of (QO) and 330 mg. of $PO(OPh)_3$, (QO), 250 mg. (83.5% recovery) was recovered. f) with $P(OPh)_3$: From 300 mg., of (QO) and 300 mg. of $P(OPh)_3$,(QO), 80 mg. (26.6% recovery) and (VII), 10 mg. (3.7% yield), were given.

Reactions of (LO)——a) with Ac_2O: From 300 mg. of (LO) and 10 cc. of Ac_2O, 4′-dimethylaminocinchoninanilide 1-oxide (XVIII), m.p. 252~253°, 160 mg. (53% yield), was obtained. IR λ_{max}^{Nujol} μ: 6.0 (amide I), 6.56 (amide II). *Anal.* Calcd. for $C_{18}H_{17}O_2N_3$: C, 70.34; H, 5.88; N, 13.67. Found: C, 70.74; H, 5.70; N, 13.59. (XVIII) was deoxygenated with PCl_3 to yield (XIII). b) with SO_2: From 700 mg. of (LO), (XI), 10 mg. (1.5% yield), and (XVIII), 220 mg (33.4% yield), were given. c) with PCl_3: From 500 mg. of (LO) and 350 mg. of PCl_3, (XIII), 130 mg. (27.4% yield), was obtained. d) with $POCl_3$: A solution of 700 mg. of (LO) and 420 mg. of $POCl_3$ was allowed to stand at room temperature for 3 hr. After a usual treatment, (XIII), 10 mg. (1.5% yield), was given. e) with $PO(OPh)_3$: From 500 mg. of (LO) and 500 mg. of $PO(OPh)_3$, a trace of (XI) and (XVI), 370 mg. (74% yleld), were given. f) with $P(OPh)_3$: From 500 mg. of (LO) and 510 mg. of $P(OPh)_3$, (LO), 110 mg. (22% recovery), (XI), 30 mg. (6.3% yield), and trace of (XVI) were obtained.

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Summary

Reactions of N-dimethylaminophenylnitrones, having either pyridine or quinoline ring, as α-substituent, with six sorts of reagent such as SO_2, $P(OPh)_3$, $PO(OPh)_3$, were examined. The observation that the deoxygenation and the rearrangement reaction of these nitrones were competitive each other confirmed the conclusion that —I effect of the heteroaromatic ring was responsible for deoxygenation and that +M effect of N-oxide group might cause rearrangement.

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