The authors are indebted to the members of the Microanalytical Center of Kyoto University for the analytical data.

Summary

Infrared spectra were applied to the studies on the amido-imido tautomerism of the sulfonamide derivatives containing the heterocyclic rings such as thiadiazole and isoxazole. 2-Phenylsulfonamidothiophene was used as a model compound of the amido-form. From the pattern of the spectral change on N-deuteration and the comparison with the corresponding carboxylic acid amides in the region 1650~1500 cm^{-1}, it was found that 2-sulfonamidothiadiazoles exist in the imido-form, while 3- and 5-sulfonamidoisoxazoles exist in the amido-form in the solid state.

For most of the sulfonamides the SO_2 symmetric stretching frequencies of the imido-form were found to be lower than those of the amido-form.

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106. Masatomo Hamana and Hiroshi Noda: Studies on Tertiary Amine Oxides. XXVII.*1 Reactions of Aromatic N-Oxides with Enamines of Cyclohexanone in the Presence of Acylating Agents. (2)*2: Reaction of α- and γ-Methyl-pyridine and -quinoline N-Oxides.

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Recently we have shown that the acyl-adducts of N-oxides of pyridine series readily react with enamines of cyclohexanone to give the corresponding 2-(α-heterocyclyl)cyclohexanones (I, II and III) in good yields after hydrolysis of the reaction mixtures.*2 In order to explore the scope and limitations of the reaction, studies were carried out with a variety of derivatives of aromatic N-oxides. The present communication describes the reactions of α- and γ-methyl-pyridine and -quinoline N-oxides with enamines of cyclohexanone in the presence of an acylating agent.

When benzoyl chloride (1.2 equiv.) was added with stirring to an ice-cooled solution of 2-picoline 1-oxide (IV) and morpholine enamine of cyclohexanone (2 equiv.) in chloroform, an exothermic reaction occurred and the solution turned to light orange. The reaction mixture was allowed to stand at room temperature for further three days, followed by treatment with 20% hydrochloric acid to afford a yellow oil as a basic fraction. It was distilled under reduced pressure to give 2-(6-methyl-2-pyridyl)cyclohexanone (VI), $b.p_{0.2}$ 115~120°, in 82% yield.

Similarly 4-picoline 1-oxide (V) gave 2-(4-methyl-2-pyridyl)-cyclohexanone (VII), $b.p_{0.12}$ 115~120°, in 72% yield.

The structures of VI and VII were deduced from their conversions by hydrogen peroxide-acetic acid oxidation to the corresponding picolinic acid 1-oxides (VIII[1] and IX)

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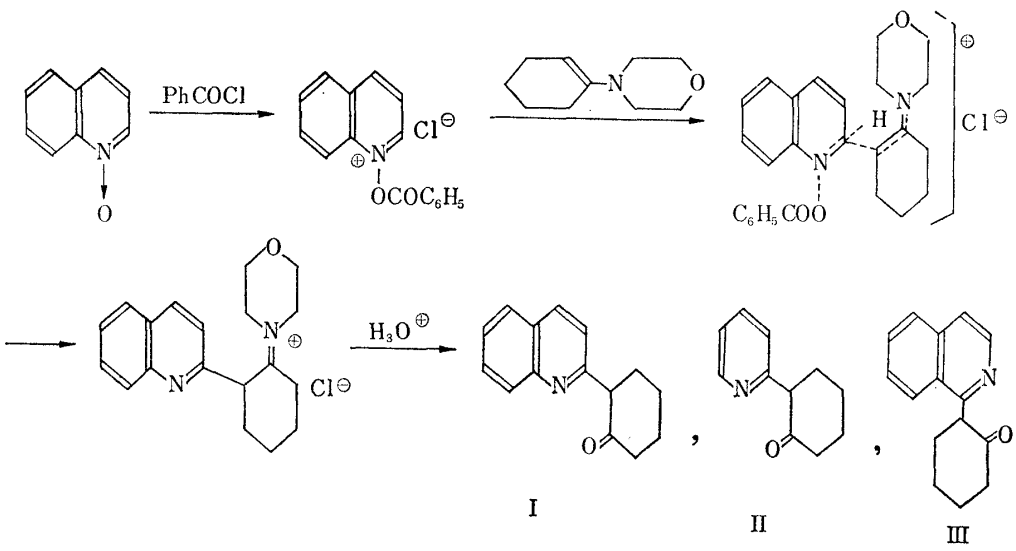
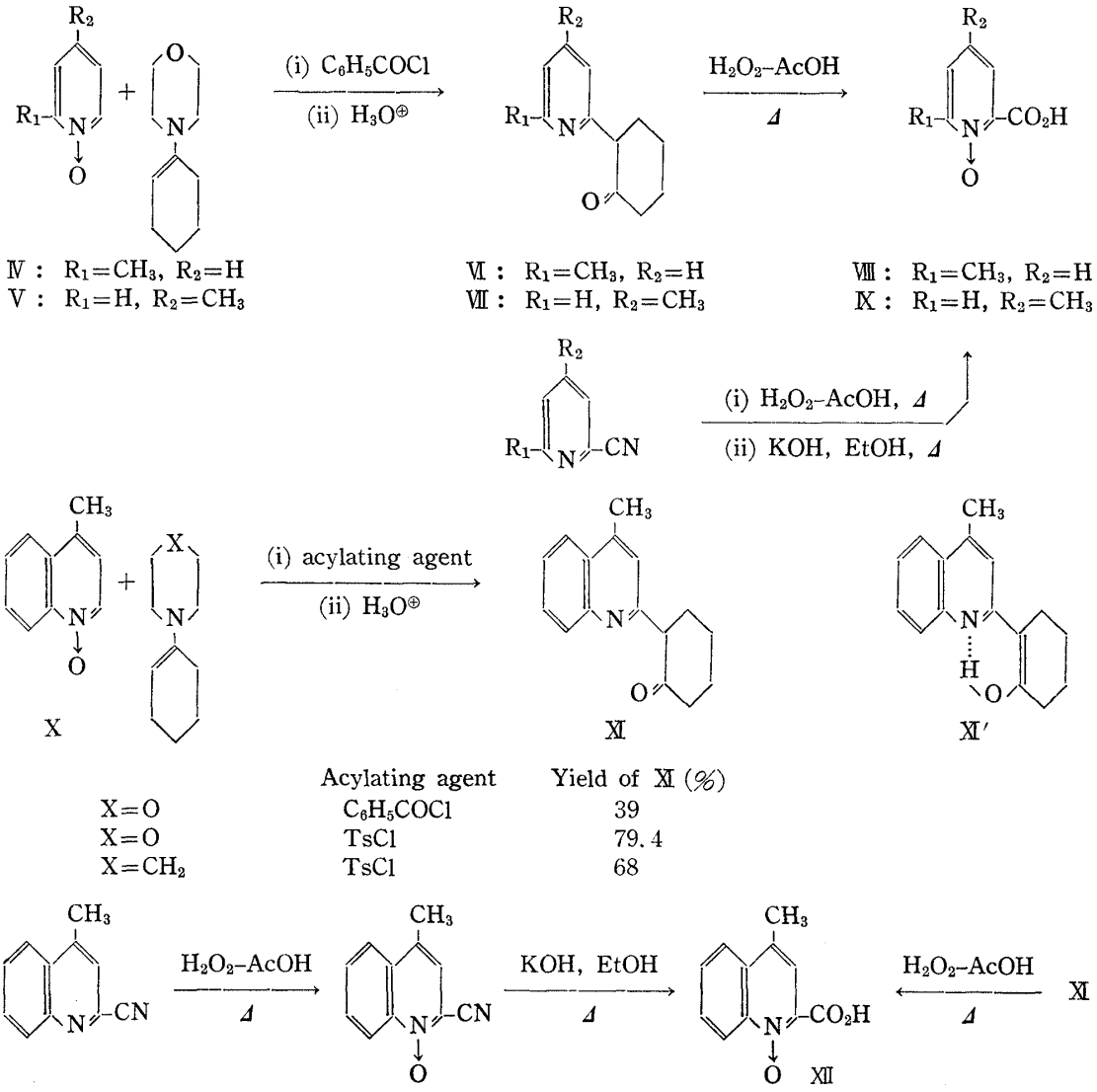
*1 Part XXVI. M. Hamana, T. Nagayoshi: This Bulletin, **14**, 319 (1966).
*2 Part I. M. Hamana, H. Noda: This Bulletin, **13**, 912 (1965).
*3 Katakasu, Fukuoka (浜名政和, 野田浩司).
1) W. Baker, K. M. Buggle, J. F. W. McOmie, D. A. M. Watkins: J. Chem. Soc., **1958**, 3594; J. Szafran: Roczniki. Chem., **38**, 1793 (1964) (C. A., **62**, 10403 (1965)).



I , II , III

respectively as described in the case of I*[2], as well as from analogy with the reaction of quinoline 1-oxide*[2] (Chart 1).



Ⅳ : $R_1=CH_3$, $R_2=H$
Ⅴ : $R_1=H$, $R_2=CH_3$

Ⅵ : $R_1=CH_3$, $R_2=H$
Ⅶ : $R_1=H$, $R_2=CH_3$

Ⅷ : $R_1=CH_3$, $R_2=H$
Ⅸ : $R_1=H$, $R_2=CH_3$

X, Ⅺ, Ⅺ′

	Acylating agent	Yield of Ⅺ (%)
X=O	C_6H_5COCl	39
X=O	TsCl	79.4
$X=CH_2$	TsCl	68

Ⅻ

Chart 1.

Lepidine 1-oxide (X) also reacted with enamines of cyclohexanone to yield 2-(4-methyl-2-quinolyl) cyclohexanone (XI), orange prisms, m.p. 101~102.5°, which was oxidized with hydrogen peroxide-acetic acid to 4-methylquinaldic acid 1-oxide (XII). In this case, noteworthily, the better result was obtained upon employing tosyl chloride than benzoyl chloride as an acylating agent. The infrared spectrum of XI in Nujol lacked any ketonic band but showed a strong absorption band at 1618 cm^{-1} attributed to an enol C=C bond; thus, XI seemed to exist predominantly as a chelated-enol form (XI') in the same manner as I*[2] (Chart 1).

Quinaldine 1-oxide (XIII) was similarly treated with the morpholine enamine (2 equiv.) and tosyl chloride (1.2 equiv.) in a chloroform solution. After the resulted orange-colored reaction mixture was kept at room temperature overnight, followed by shaking with 20% hydrochloric acid, the chloroform layer (Ext. I) was separated from the acidic solution, which was basified with solid potassium carbonate and extracted again with chloroform (Ext. II). From Ext. I were isolated colorless needles (XIVa) of m.p.117~118.5° (47% as $C_{17}H_{15}O_3NS$) and a white powder (XV) of m.p. 235~237° (17.2% as $C_{16}H_{17}ON \cdot C_7H_8O_3S$); from Ext. II colorless needles (XIVb) of m.p. 64~66° (2.7% as $C_{10}H_8NCl$) and colorless pillars (XVI) of m.p. 106~106.5° (21% as $C_{16}H_{17}ON$) were obtained.

Treatment of XV with potassium carbonate solution gave XVI, which being reversely transformed into XV with an equivalent amount of *p*-toluenesulfonic acid in ethanol. These facts obviously showed that XV was *p*-toluenesulfonate of XVI. The infrared spectrum of XVI exhibited a strong absorption band at 1704 cm^{-1} characteristic of a six-membered ketone, and its ultraviolet spectrum in ethanolic solution is slightly different from that of quinaldine, although both spectra in ethanolic hydrochloric acid are practically the same (Fig. 1 a,b). The nuclear magnetic resonance (NMR) spectrum of XVI in deuteriochloroform shows a signal (three protons, singlet) attributable to the 2-methyl group of quinoline nucleus at 7.29τ, complex signals from 7.3 to 8.5τ due to eight protons of the methylene groups of cyclohexanone ring, and a complex, broad peak at 5.7τ due to a single proton attributable to the methyne group. In the region of aromatic protons, XVI gives a peak at 2.88τ (the proton of 3-position of quinoline ring) and complex signals from 2.2 to 2.8τ due to three protons (protons of 5, 6, and 7-positions of quinoline ring), however, at near 2τ is observed a signal due to only one proton (proton of 4- or 8-position of quinoline nuclei). These facts suggest that XVI is probably 2-(2-methyl-4- or 8-quinolyl) cyclohexanone.

Reduction of XVI with sodium borohydride afforded an alcohol of m.p. 199~200.5° (XVII) in a good yield. When XVII was subjected to dehydration by heating at 140~150° with 70% sulfuric acid in the presence of a minute amount of hydroquinone, the reaction was unexpectedly accompanied by further dehydrogenation and 4-phenylquinaldine (XVIII)[3] was resulted. The yield of XVIII was markedly dependent on the reaction conditions as shown in Table I. The constitution of XVIII was established by direct comparison with an authentic specimen prepared by another route.[2] From the result mentioned above XVI was proved to be 2-(2-methyl-4-quinolyl)cyclohexanone.

XIVa gave a positive sulfur test and showed infrared absorption bands at 1377 and 1193 cm^{-1} characteristic of a sulfonyloxy group. When heated under reflux with ethanolic potassium hydroxide, XIVa yielded 3-hydroxyquinaldine,[3] which was proved to be identical with an authentic sample prepared by an independent method. Thus, XIVa was identified as 3-tosyloxyquinaldine.

XIVb contains a chlorine atom and the melting points of XIVb and its picrate agreed with those[4] reported for 3-chloroquinaldine and its picrate, respectively. Furthermore,

2) C. Beyer: Ber., **20**, 1770 (1887); E. Knövenagel: *Ibid.*, **55**, 1929 (1922).
3) W. Koenigs, F. Stockhausen: Ber., **35**, 2554 (1902); H. Tanida: This Bulletin, **5**, 188 (1957).
4) G. Magnanini: Ber., **20**, 2608 (1887); A. Busch, W. Koenigs: *Ibid.*, **24**, 3963 (1891).

its NMR spectrum in deuteriochloroform has a sharp peak at 7.2τ (3H; 2-methyl group of quinoline ring), and does not show a signal attributable to the proton attached to the 3-position of quinoline ring. Therefore, XIVb is considered to be 3-chloroquinaldine (Chart 2).

Curiously, the use of benzoyl chloride as an acylating agent in the reaction of XIII led to the formation of a complex mixture of untractable products.

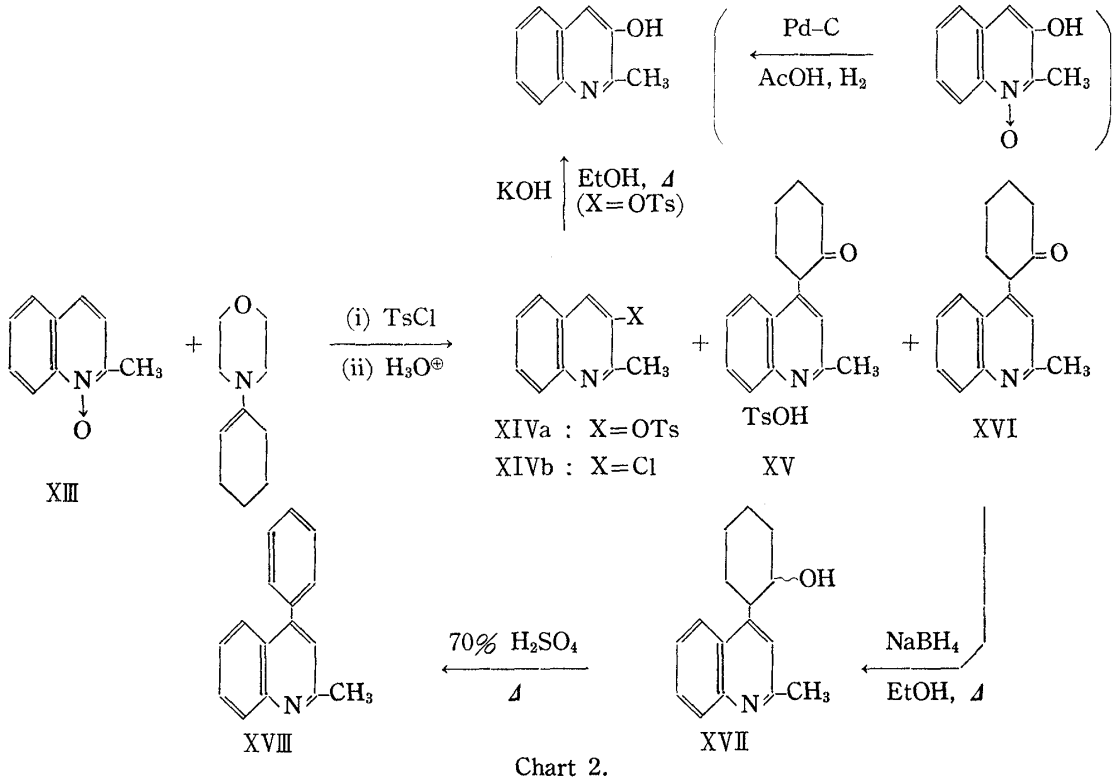


Chart 2.

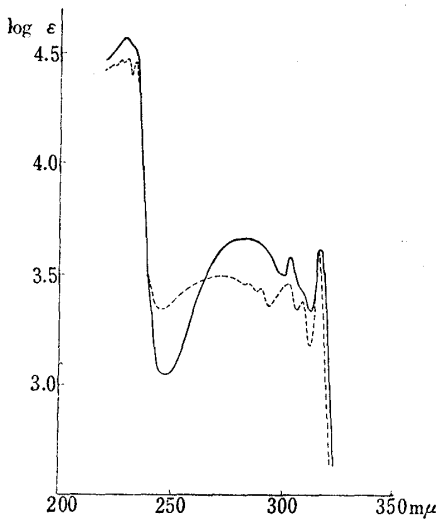


Fig. 1a. Ultraviolet Spectra in Ethanol

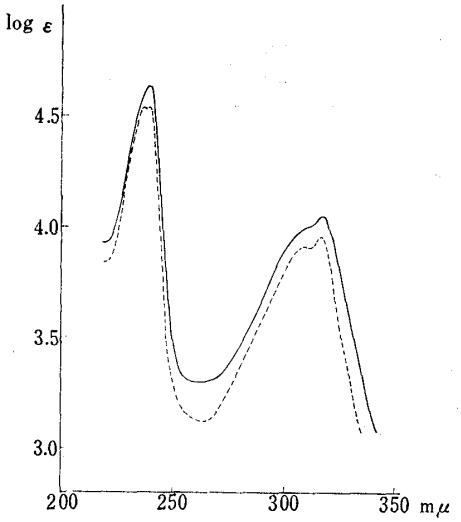


Fig. 1b. Ultraviolet Spectra in Ethanol Containing 0.1 Volume of Conc. Hydrochloric Acid

——— 2-(2-Methyl-4-quinolyl)cyclohexanone (XVI)
- - - - - - Quinaldine

The results mentioned above indicate that the active methyl group does not participate in the reaction and nucleophilic attack by the enamine always occurs at the nucleus, that is, at the α- or γ-position to the N-oxide function. These reactions may be considered to proceed by the addition-elimination mechanism in the similar way as those of quinoline and pyridine N-oxides.*2

The results obtained in the cases of 2-picoline, 4-picoline and lepidine N-oxides, in which at least one of the α-position to the N-oxide function has no substituent, can be reasonably understood in view of the great susceptibility of the α-position to this type of substitution.*2 The influence of methyl group is, however, apparently noticed in the case of lepidine 1-oxide; that is, tosyl chloride is more effective than benzoyl chloride as acylating agent, which fact is contrary to the observations obtained in the reaction of quinoline and pyridine N-oxides.*2 This may be ascribed to the electron-releasing effect of 4-methyl group, which decreases to a fairly extent the electrophilic character of the 2-position of quinoline ring,[5] so that a more powerful electron-attracting ability of the acyl group bound to N-oxide function would be required for the smooth progress of the reaction.

On the other hand 3-tosyl-(XIVa) and 3-chloro-quinaldine (XIVb) were obtained in addition to 2-(2-methyl-4-quinolyl)cyclohexanone (XVI) from quinaldine 1-oxide (XIII). The formation of XIVa and XIVb, which is similar to some reactions between aromatic

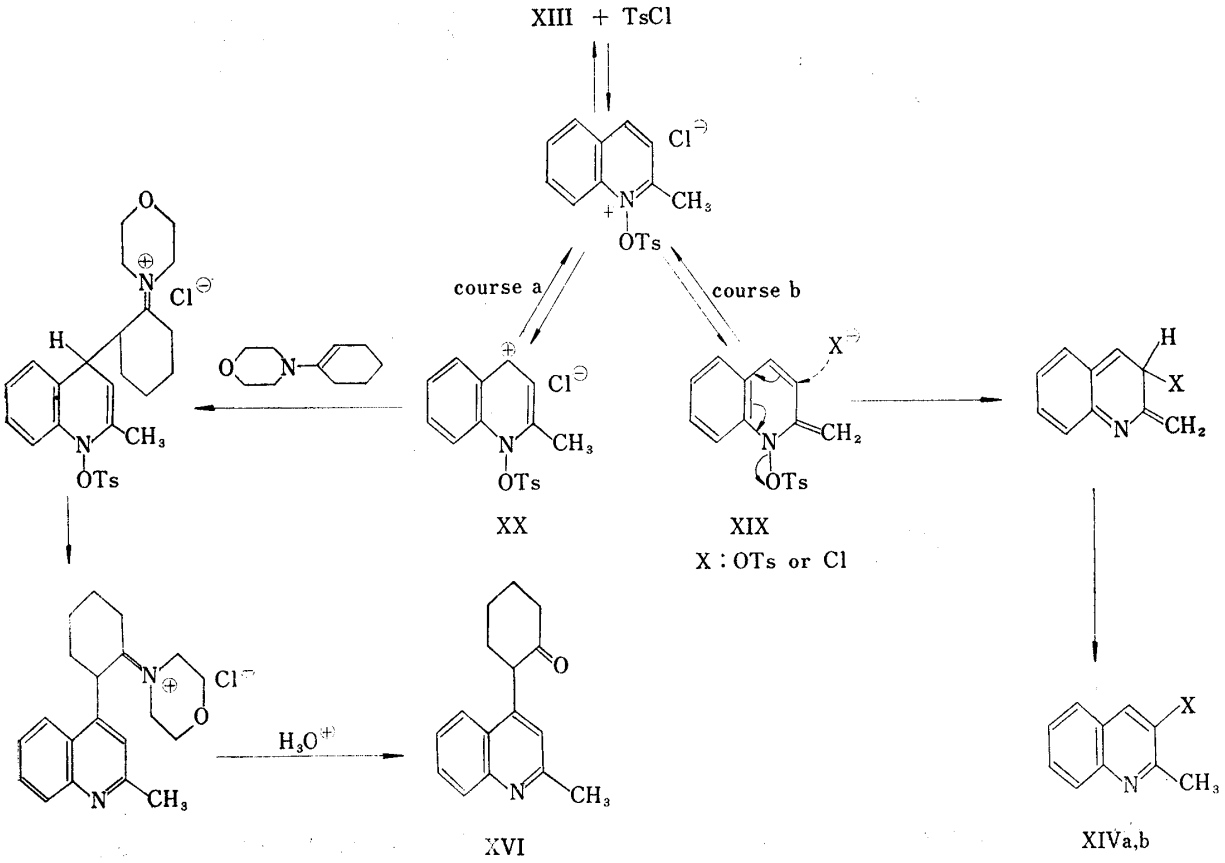


Chart 3.

5) M. Hamana, M. Yamazaki: This Bulletin, **10**, 51 (1962); **11**, 415 (1963).

N-oxides containing an active methyl group and acylating agent,[6] may be probably rationalized by the mechanism (course b) involving the anhydrobase (XIX).*4 It is very remarkable that in spite of the possibility of this course (b) the enamine was introduced exclusively into the 4-position by the addition-elimination mechanism (course a) with no visible signs of attack at 2-methyl group or the 3-position (Chart 3). Although this fact seems to indicate one of the characteristics of the reaction of aromatic N-oxide with enamine, the correlation between positional selectivity and the nature of entering group is not clear at present and remains to be elucidated.

Experimental*5

1) **Reaction of 2-Picoline 1-Oxide (IV)**——To an ice-cooled solution of IV (2.18 g.) and morpholine enamine of cyclohexanone (6.68 g.) in $CHCl_3$ (20 ml.), C_6H_5COCl (3.4 g.) was added with stirring. After standing at room temperature for 3 days, the mixture was treated with 20% HCl (40 ml.) and concentrated *in vacuo*. The residue was dissolved in 5% HCl, washed with ether-benzene, basified with solid K_2CO_3 and extracted with $CHCl_3$. The extract on evaporation gave 2-(6-methyl-2-pyridyl)cyclohexanone (VI) as a yellow oil, $b.p_{0.2}$ 115~120°. *Anal.* Calcd. for $C_{12}H_{15}ON$: N, 7.40. Found: N, 7.37.

2) **Oxidation of VI to 6-Methylpicolinic Acid 1-Oxide (VIII)**——A mixture of VI (1 g.) and 30% H_2O_2 (15 ml.) in AcOH (30 ml.) was warmed at 70~80°. After 2 and 6 hr., respectively 15 and 10 ml. of H_2O_2 were added, and the solution was kept at the same temperature further 8 hr. The reaction mixture was evaporated *in vacuo* to dryness, followed by extraction with $CHCl_3$. The solvent was removed and the residue was recrystallized from EtOH to afford 0.45 g. of VIII,[1] colorless needles, m.p. 174~176°(decomp.), which was identified by comparison with a sample prepared by the method described below. *Anal.* Calcd. for $C_7H_7O_3N$: C, 54.90; H, 4.61; N, 9.15. Found: C, 55.21; H, 4.19; N, 9.31.

3) **Preparation of 6-Methylpicolinic Acid 1-Oxide (VIII)**[1]——A solution of 6-methylpicolinonitrile[8] (0.45 g.) and 30% H_2O_2 (10 ml.) in AcOH (20 ml.) was heated at 80~90° on a water bath for 3 hr., and then further 10 ml. of H_2O_2 was added, the heating being continued for 9 hr. The reaction mixture was concentrated *in vacuo*, the residue was dissolved in H_2O, made alkaline with solid K_2CO_3 and extracted with $CHCl_3$. Evaporation of the solvent gave a solid, which was recrystallized from EtOH to give 0.21 g. of colorless pillars. This was refluxed for 11 hr. with a mixture of 10% NaOH (7.5 ml.) and EtOH (15 ml.) and then concentrated *in vacuo*. The residue was dissolved in H_2O, weakly acidified with dil. HCl, and the resultant deposits were collected, recrystallized from EtOH to afford 0.225 g. of VIII, colorless needles, m.p. 174~175°(decomp.).

4) **Reaction of 4-Picoline 1-Oxide (V)**——The experiment was carried out as described in 1), using 1.1 g. of V, 3.68 g. of the morpholine enamine, 1.7 g. of C_6H_5COCl and 10 ml. of $CHCl_3$. 2-(4-Methyl-2-pyridyl)cyclohexanone (VII) was obtained as a pale yellow oil, $b.p_{0.12}$ 115~120°: yield, 1.36 g. Picrate: m.p. 160~162°, yellow fine needles (EtOH). *Anal.* Calcd. for $C_{12}H_{15}ON \cdot C_6H_3O_7N_3$: C, 51.67; H, 4.34; N, 13.39. Found: C, 52.08; H, 4.45; N, 13.70.

5) **Oxidation of VII to 4-Methylpicolinic Acid 1-Oxide (IX)**——Oxidation of VII (1 g.) with 30% H_2O_2 (30 ml.) in AcOH (30 ml.) yielded 0.49 g. of IX, m.p. 164~166°((decomp.) (EtOH). *Anal.* Calcd. for $C_7H_7O_3N$: C, 54.90; H, 4.61; N, 9.15. Found: C, 55.20; H, 4.72; N, 9.52. An authentic sample of IX was prepared from 4-methylpicolinonitrile[8] as described for VIII.

6) **Reaction of Lepidine 1-Oxide (X)**——A solution of X (1.59 g.) and the morpholine enamine (3.68 g.) in $CHCl_3$ (10 ml.) was treated with TsCl (2.29 g.) under ice-cooling and stirring. After standing overnight at room temperature, the reaction mixture was worked up as 1). The crude product was purified by chromatography in benzene on alumina to afford 1.89 g. of 2-(4-methyl-2-quinolyl)cyclohexanone (XI), orange prisms, m.p. 101~102.5°(MeOH). *Anal.* Calcd. for $C_{16}H_{17}ON$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.24; H, 7.26; N, 5.82. Oxime: colorless prisms, m.p. 184~186°(EtOH). *Anal.* Calcd. for $C_{16}H_{18}ON_2$: C, 75.56; H, 7.13; N, 11.02. Found: C, 75.47; H, 7.04; N, 11.06.

7) **Oxidation of XI to 4-Methylquinaldic Acid 1-Oxide (XII)**——Oxidation of XI (0.48 g.) with 30%

*4 The formation of XIVa is apparently intermolecular, but the detailed mechanism of that of XIVb is not yet clear, although an intramolecular rearrangement of tosyloxy group seems preferable rather than an intermolecular reaction.[7]

*5 All melting and boiling points were uncorrected.

6) G. Kobayashi, S. Furukawa: This Bulletin, **1**, 347 (1953); V. Boekelheide, W. J. Linn: J. Am. Chem. Soc., **76**, 1286 (1954); E. Ochiai: Ann. Rep. ITSUU Lab. (Tokyo), **12**, 43 (1962); S. Oae, Y. Kitaoka, T. Kitao: J. Am. Chem. Soc., **84**, 3359, 3362 (1962); *Idem*: Tetrahedron, **20**, 2685 (1964) and papers quoted therein.

7) S. Oae, T. Kitao, Y. Kitaoka: Tetrahedron, **19**, 827 (1963).

8) T. Okamoto, H. Tani: This Bulletin, **7**, 925 (1959).

H_2O_2–AcOH as described in 2) furnished 0.22 g. of XII, colorless or pale yellow needles, m.p. 174~175° (decomp.) (MeOH). *Anal.* Calcd. for $C_{11}H_9O_3N$: C, 65.02; H, 4.46; N, 6.89. Found: C, 64.97; H, 4.55; N, 6.53. This was shown to be identical with an authentic sample prepared by the procedure described below by admixture and comparison of their IR spectra.

4-Methylquinaldonitrile[9] (1 g.) was oxidized in the usual way with 30% H_2O_2–AcOH to 4-methylquinaldonitrile 1-oxide (0.85 g.), pale yellow prisms, m.p. 179~181°(EtOH). *Anal.* Calcd. for $C_{11}H_8ON_2$: C, 71.72; H, 4.38; N, 15.21. Found: C, 71.63; H, 4.52; N, 15.18. The N-oxide (0.3 g.) were refluxed with a mixture of 2*N* KOH (3 ml.) and EtOH (18 ml.) for 15 hr. The solvent was removed under reduced pressure, the residue taken up in H_2O and made weakly acidic with dil. HCl to precipitate crystals, which was collected, washed with H_2O and recrystallized from MeOH to give 0.29 g. of XII, pale brown needles, m.p. 174~175° (decomp.). *Anal.* Calcd. for $C_{11}H_9O_3N$: N, 6.89. Found: N, 6.94.

8) **Reaction of Quinaldine 1-Oxide (XIII)**——To an ice-cooled solution of XIII (3.18 g.) and the morpholine enamine (7.36 g.), TsCl (4.58 g.) was added with stirring and the whole was kept standing overnight at room temperature. After the reaction mixture was occasionally shaken with 20% HCl (40 ml.) during a period of 1.5 hr., $CHCl_3$ layer was separated and aqueous layer was further extracted with $CHCl_3$ (the combined $CHCl_3$ extract=Ext. I). The acidic solution was basified with solid K_2CO_3 and extracted with $CHCl_3$ (Ext. II).

Removal of the solvent from Ext. I left a solidified residue which was treated with as small amount of cold EtOH as possible. Undissolved crystals were collected and recrystallized from EtOH to afford 1.41 g. of colorless powder (XV), m.p. 235~237°. *Anal.* Calcd. for $C_{16}H_{17}ON \cdot C_7H_8O_3S$: C, 67.14; H, 6.12; N, 3.40. Found: C, 66.86; H, 6.19; N, 3.63. The alcoholic filtrate from XV was evaporated, the residue was taken up in benzene and passed through an alumina column to give 2.94 g. of colorless needles (XIVa), m.p. 117~118.5°(EtOH). *Anal.* Calcd. for $C_{17}H_{15}O_3NS$: C, 65.17; H, 4.82; N, 4.47. Found: C, 65.11; H, 4.75; N, 4.63.

The solvent was removed from Ext. II, the residue was chromatographed on alumina using petr. ether and then ether for elution. The first fraction afforded colorless needles (XIVb) (0.22 g. as its picrate, m.p. 222~224°), m.p. 64~66°, $b.p_5$ 110~120°(bath. temp.). *Anal.* Calcd. for $C_{10}H_8NCl$: C, 67.61; H, 4.54; N, 7.89. Found: C, 67.59; H, 4.50; N, 7.74. Picrate, *Anal.* Calcd. for $C_{10}H_8NCl \cdot C_6H_3O_7N_3$: C, 47.24; H, 2.73; N, 13.76. Found: C, 47.61; H, 2.99; N, 13.94. The second was recrystallized from petr. ether or isopropyl ether to yield 1 g. of colorless pillars (XVI), m.p. 106~106.5°. *Anal.* Calcd. for $C_{16}H_{17}ON$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.67; H, 7.06; N, 5.57. UV λ_{max}^{EtOH} mμ (log ε): 230 (4.57), 233 (4.53) (inflec.), 280 (3.66), 305 (3.57), 308 (3.45) (inflec.), 318 (3.60). $\lambda_{max}^{EtOH\text{-}HCl}$ *6 mμ (log ε): 239.5 (4.63), 310 (3.99) (inflec.), 318 (4.05).

9) **Reactions of XVI and XIV**——i) XVI (0.12 g.) and TsOH (monohydrate 0.1 g.) were combined in hot EtOH. After cooling 0.2 g. of XV was deposited from the solution.

ii) A solution of XVI (0.36 g.) and $NaBH_4$ (0.09 g.) in EtOH (10 ml.) was refluxed for 2.5 hr. The crude product was recrystallized from benzene to give 0.32 g. of the corresponding alcohol (XVII), colorless crystals, m.p. 199~200.5°. *Anal.* Calcd. for $C_{16}H_{19}ON$: C, 79.63; H, 7.94; N, 5.80. Found: C, 79.76; H, 7.95; N, 5.82.

XVII (0.45 g.) and hydroquinone (15 mg.) were dissolved in 70% sulfuric acid (10 ml.), and the mixture was heated at 140~150° for 8 hr. After cooling, the dark solution was poured into ice-water, neutralized with conc. NH_4OH, and extracted with $CHCl_3$. The $CHCl_3$ solution was evaporated, and the residue was purified by chromatography in benzene on alumina followed by recrystallization from *n*-hexane to give 0.25 g. of colorless prisms, m.p. 99~101°. *Anal.* Calcd. for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.60; H, 5.88; N, 6.30. Picrate: yellow plates, m.p. 205~207°(MeOH). *Anal.* Calcd. for $C_{16}H_{13}N \cdot C_6H_3O_7N_3$: C, 58.93; H, 3.60; N, 12.50. Found: C, 58.94; H, 3.82; N, 12.75. These were proved to be identical with authentic samples of 4-phenylquinaldine[2] by comparison of their melting points and IR spectra.

Table I. Reaction of XVII with 70% Sulfuric Acid

XVII (g.)	70% H_2SO_4 (ml.)	Hydroquinone (mg.)	Reaction conditions		4-Phenylquinaldine yield (g.) (%)
			temp. (°C)	time (hr.)	
0.3	6	12	155~165	8	0.11 (40.4)
0.45	10	15	140~150	8	0.25 (60.4)
0.5	10	20	120~130	8	0.06 (13.2)

iii) A mixture of XIVa (0.63 g.) and KOH (2 g.) in EtOH (18 ml.) was refluxed for 3 hr. After removing EtOH, the residue was dissolved in H_2O, followed by saturation with NH_4Cl. The resulted precipitates were

*6 EtOH containing 0.1 volume of conc. HCl.

9) E. Ochiai, I. Nakayama: Yakugaku Zasshi, **65B**, 582 (1945).

collected, washed with H_2O and recrystallized from acetone to yield 0.39 g. (94%) of 3-hydroxyquinaldine, colorless needles, m.p. 259~262°(decomp.). *Anal.* Calcd. for $C_{10}H_9ON$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.13; H, 6.00; N, 8.94. This was identified by direct comparison with an authentic sample.[3]

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Summary

Reactions of α- and γ-methyl-pyridine and -quinoline N-oxides with enamines of cyclohexanone in the presence of an acylating agent were examined. From N-oxides of 2-picoline (IV), 4-picoline (V) and lepidine (X), the corresponding 2-(2-heterocyclyl)-cyclohexanones (VI, VII, XI) were obtained in good yields. The reaction of quinaldine 1-oxide (XIII) followed two kinds of courses, producing 2-(2-methyl-4-quinolyl)cyclohexanone (XV, XVI; 38.2%) accompanied with 3-tosyloxy-(XIVa; 47%) and 3-chloroquinaldine (XIVb; 2.7%).

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