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Studies on Tertiary Amine Oxides. LXXVI.[1] Reactions of Aromatic *N*-Oxides with 1,3-Cyclohexanediones in the Presence of Acetic Anhydride

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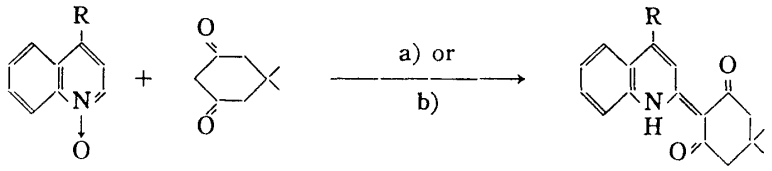
Quinoline 1-oxides (**1a**—**c**) readily reacted with dimedone (**2**) and 1,3-cyclohexanedione (**10**) in acetic anhydride or in dimethylformamide (DMF)-containing 1.2 eq of acetic anhydride to afford the corresponding 2-substituted quinolines (**3a**—**c** and **11a**—**c**). The reaction of 3-bromoquinoline 1-oxide (**1d**) with **2** in DMF-acetic anhydride gave the 2-substituted quinoline (**3d**), whereas that in acetic anhydride alone afforded the enol acetate of **3d** (**3d'**). The reactions of isoquinoline 2-oxide (**5**) with **2** and **10** similarly gave the 1-substituted isoquinolines (**6** and **12**). While pyridine 1-oxide (**7**) reacted with **2** to give the 2-substituted pyridine (**8**), the reaction with **10** produced 3-(2,6-dioxocyclohexylidene)-2-(4-pyridyl)cyclohexanone (**13**).

Keywords——aromatic *N*-oxide; dimedone; 1,3-cyclohexanedione; 2-(2-quinolyl)-cyclohexane-1,3-dione; 2-(1-isoquinolyl)cyclohexane-1,3-dione; 5,5-dimethyl-2-(2-pyridyl)cyclohexane-1,3-dione; 3-(2,6-dioxocyclohexylidene)-2-(4-pyridyl)cyclohexanone; nucleophilic reaction

It was reported many years ago that quinoline 1-oxide readily reacts with 1,3-indanedione in the presence of acetic anhydride to give 2-(2-quinolyl)indanedione in good yield,[3] but no reports are available on the reaction of aromatic *N*-oxide with other cyclic β-diketones. Recently, we found that the reactions of quinoline 1-oxides with Meldrum's acid in acetic anhydride gave 5-(2-quinolyl)-Meldrum's acids in the usual way, whereas the reactions in dimethylformamide containing 1.2 equivalents of acetic anhydride afforded the corresponding quinolinium-5-Meldrum's acid ylides as the main products.[1] These results promopted us to investigate the reactions of *N*-oxides of quinolines, isoquinoline and pyridine with dimedone and 1,3-cyclohexanedione in the presence of acetic anhydride.

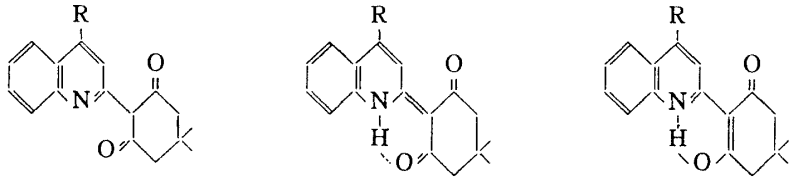
When quinoline 1-oxide (**1a**) was treated with dimedone (**2**) in an excess of acetic anhydride at 90°C for 8 h [conditions a)], a yellow solution was formed and 5,5-dimethyl-2-(2-quinolyl)-cyclohexane-1,3-dione, 4-(2-quinolyl)dimedone (**3a**), was obtained in 75% yield. The reaction in dimethylformamide (DMF) containing 1.2 equivalents of acetic anhydride at 90°C for 8 h [conditions b)] also gave **3a** as the sole product in 79% yield, no ylide formation being noted.[1,4] Quite similarly, lepidine and 4-chloroquinoline 1-oxides (**1b** and **1c**) readily reacted with **2** under both conditions, and the corresponding 2-substituted quinolines (**3b** and **3c**) were formed in good yields. On the other hand, treatment of 3-bromoquinoline 1-oxide (**1d**) with **2** under conditions a) resulted in the formation of the enol acetate of the 2-substituted quinoline (**3d'**) in 87% yield. However, when the reaction was carried out under conditions b), 4-(3-bromo-2-quinolyl)dimedone (**3d**) was obtained in 83% yield. Thus, *N*-ylide formation was again not observed in the reaction of **1d** in spite of the fact that the reaction of **1d** with Meldrum's acid gives only the *N*-ylide independently of the reaction conditions[4] (Chart 1 and Tables I and II).

The analytical values and the spectral data of these products were in full agreement with the proposed structures (Tables I and II). The infrared (IR) spectra of **3a**—**c** exhibited strong carbonyl bands at 1630—1650 cm^{-1} as well as NH absorptions in the 3100—3180 cm^{-1} region, but lacked absorptions in the 2400—2600 cm^{-1} region due to chelated enolic OH groups. Their nuclear magnetic resonance (NMR) spectra in deuteriochloroform showed NH resonance signals

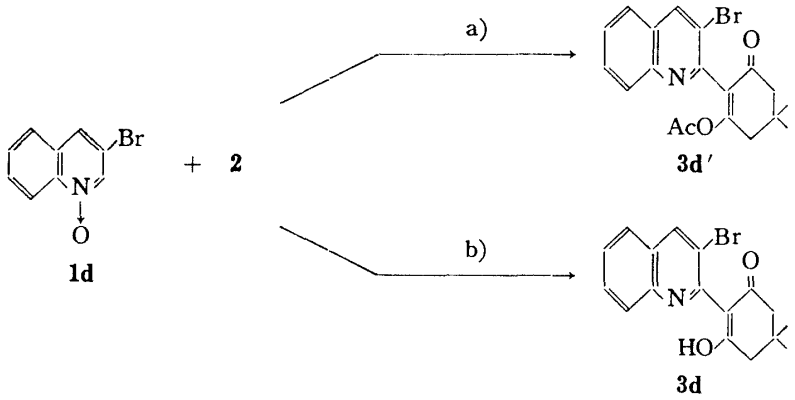


1a—c **2** **3a—c**

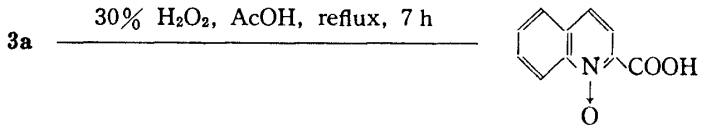
a: R=H, **b**: R=Me, **c**: R=Cl



3-A **3-B** **3-C**



1d **3d′** **3d**



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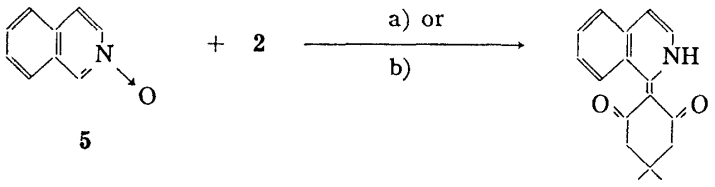
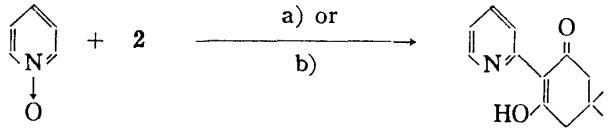
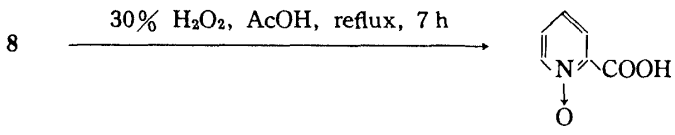


5 **6**



7 **8**



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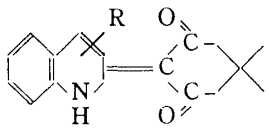
Conditions a) heated at 90°C for 8 h in Ac_2O
b) heated at 90°C for 8 h in Ac_2O(1.2 eq)-DMF

Chart 1

Table I. 2-(2-Quinolyl)dimedones (**3a—d**)



3a—d

Compound No.	R	Yield (%)	Appearance	mp °C	MS M^+ (*m/e*)	Formula	Analyses (%) Calcd (Found) C	H	N
3a	H	75[a] 79[b]	Yellow needles	186—187	267	$C_{17}H_{17}NO_2$	76.38 (76.35	6.41 6.49	5.24 5.26)
3b	4-Me	59[a] 63[b]	Yellow prisms	141—142	281	$C_{18}H_{19}NO_2$	76.84 (76.67	6.81 6.95	4.98 4.98)
3c	4-Cl	68[a] 71[b]	Yellow needles	167—168	301, 303	$C_{17}H_{16}ClNO_2$	69.97 (69.78	5.48 5.35	4.80 4.75)
3d	3-Br	83[b]	Pale yellow needles	249—250	345, 250	$C_{17}H_{16}BrNO_2$	58.95 (58.93	4.63 4.67	4.04 4.01)

a) The reaction was carried out in Ac_2O at 90°C for 8 h.
b) The reaction was carried out in DMF–Ac_2O at 90°C for 8 h.

Table II. IR and NMR Data for 2-(2-Quinolyl)dimedones (**3a—d**)

Compound No.	IR (cm^{-1}, Nujol) C=O	NH	NMR ($CDCl_3$, δ) C_4–H	C_3–H	Ar–H containing CH–	NH[a]	CH_3	CH_2
3a	1650	3100	8.10 (1H, d, J= 10 Hz)	9.26 (1H, d, J= 10 Hz)	7.30—7.70 (4H, m)	17.90 (1H, br s)	1.12 (6H, s)	2.52 (4H, s)
3b	1625	3160		9.10 (1H, s)	7.20—7.90 (4H, m)	17.4 (1H, br s)	1.12 (6H, s)	2.52 (4H, s)
3c	1630	3150		9.40 (1H, s)	7.40—8.08 (4H, m)	18.0 (1H, br s)	1.15 (6H, s)	2.50 (4H, s)
3d	1558		8.52 (1H, s)		7.40—8.10 (5H, m)		1.99 (6H, s)	2.52 (4H, s)

a) Each proton was exchangeable with deuterium oxide.

as one-proton broad singlets exchangeable with deuterium oxide at δ 17.40—18.0, but no signals due to the C_2-proton of the quinoline ring were noticed. These observations indicate that **3a—c** exist predominantly as the enamine forms (**3-B**), the ketonic (**3-A**) or the enol forms (**3-C**) being negligible. On the other hand, any absorption or signal due to an NH group was not noticed in the IR or NMR spectrum of **3d**, indicating that **3d** does not exist as the enamine form, in contrast to **3a—c**. It appears likely that the 3-bromo group hinders sterically the formation of the coplanar enamine form in the case of **3d**, and this situation may be correlated with the formation of the enol acetate, **3d'**, in the reaction of **1d** in excess acetic anhydride. However, the details of the configuration of **3d** cannot be elucidated from the spectral data,[5] although the enolic form seems to be preferred to the diketone form.

Oxidation of **3a** with excess 30% hydrogen peroxide in refluxing acetic acid for 7 h gave quinalidic acid 1-oxide (**4**) in 74% yield.

In the same way, isoquinoline 2-oxide (**5**) readily reacted with **2** under both conditions to afford 4-(1-isoquinolyl)dimedone (**6**) in good yields (100 and 69%, respectively). The IR and NMR spectra of **6** demonstrate that **6** exists predominantly as the enamine form in the same way as **3a—c**.

The reactivity of pyridine 1-oxide (**7**) was found to be somewhat lower than that of **1** or **5**, but the reactions with **2** under both conditions gave 4-(2-pyridyl)dimedone (**8**) in 48 and 45% yields, respectively. A strong carbonyl band in the IR spectrum at 1635 cm^{-1} indicates that **8** exists as the enol or the enamine form. While the enol form seems to be more favorable,[6] the details of its configuration could not be elucidated because of failure to detect any definite absorption or signal due to an OH or NH group in the IR and NMR spectra.

Oxidation of **8** with excess 30% hydrogen peroxide in refluxing acetic acid for 7 h gave picolinic acid 1-oxide (**9**) in 56% yield.

Subsequently, the reaction with 1,3-cyclohexanedione (**10**) was examined.

Reactions of **1a—c** with **10** in acetic anhydride at 90°C proceeded in a similar manner to those with **2**, and the corresponding 2-(2-quinolyl)cyclohexane-1,3-diones (**11a—c**) were obtained in 64, 58 and 65% yields, respectively, after heating for 8 h (Chart 2 and Table III).

The IR and NMR spectra of **11a—c** showed that **11a—c** all exist predominantly as the enamine forms (Table IV). Oxidation of **11a** with 30% hydrogen peroxide in refluxing acetic acid for 7 h gave also **4** in 69% yield.

A similar treatment of isoquinoline 2-oxide **5** with **10** for 8 h followed by concentration of the reaction mixture under reduced pressure gave an oily residue, which was solidified to yellow needles (**12**) on trituration with methanol. The analytical values ($C_{16}H_{17}NO_3$) and the MS

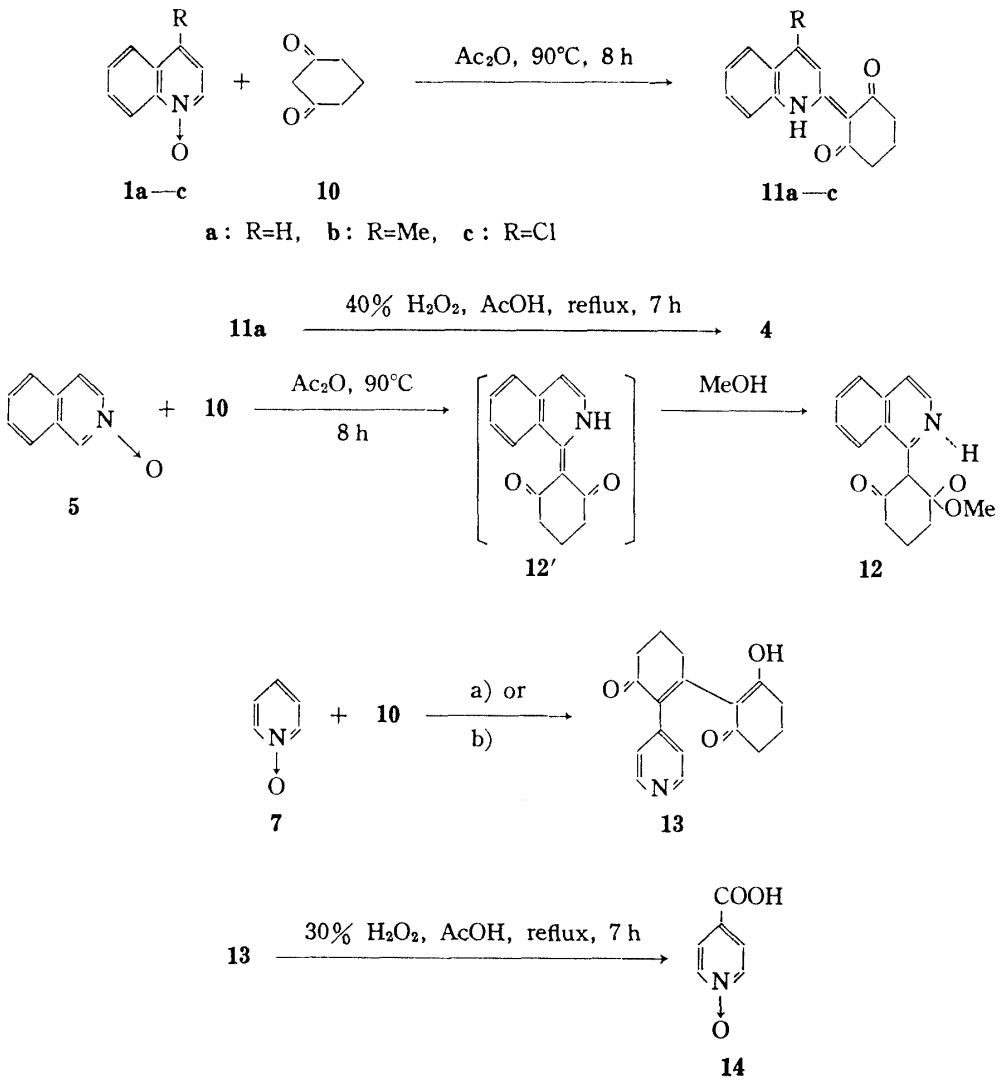


Chart 2

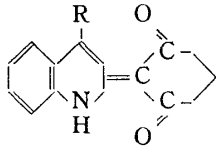
(M^+: *m/e* 271) indicated that **12** is not a usual 1-substituted isoquinoline (**12'**) but its adduct with one mole of methanol.

The IR spectrum of **12** displayed a strong carbonyl band at 1720 cm^{-1} and a weak absorption indicative of an OH group at near 2400 cm^{-1}. The NMR spectrum in deuteriochloroform showed a two-proton quintet at δ 2.06 and a four-proton triplet at δ 2.42, which could be assigned to the C_5-methylene and the C_4- and C_6-methylenes of the cyclohexanone side chain of **12**, respectively. Further, methoxy protons appeared as a three-proton singlet at δ 3.65, and a hydroxy proton was observed as a one-proton singlet exchangeable with deuterium oxide at δ 15.85.

These observations indicate that **12** has the structure shown in Scheme 2, which is apparently formed by addition of one mole of methanol to the usual product (**12'**) during work-up. Its yield was 73%. Hydrolysis of **12** to **12'** has not been attempted yet.

It was further found that the reaction of pyridine 1-oxide **7** with **10** under both conditions resulted in the formation of a 4-substituted pyridine derivative, 3-(2,6-dioxocyclohexylidene)-2-(4-pyridyl)cyclohexanone (**13**), in 39 and 32% yields, respectively. The identity of **13** was established by elemental analysis, spectral examinations and oxidation to isonicotinic acid 1-oxide (**14**) by treatment with 30% hydrogen peroxide in acetic acid under reflux for 7 h (Chart 2).

Table III. 2-(2-Quinolyl)-1,3-cyclohexanediones (**11a—c**)



11a—c

Compound No.	R	Yield (%)	Appearance	mp °C	MS M^+ (*m/e*)	Formula	Analyses (%) Calcd (Found) C	H	N
11a	H	64	Yellow needles	145	239	$C_{15}H_{13}NO_2$	75.30 (75.17	5.48 5.49	5.85 5.84)
11b	Me	58	Yellow needles	178—179	253	$C_{16}H_{15}NO_2$	75.87 (75.95	5.97 6.10	5.53 5.65)
11c	Cl	65	Brown scales	173—174	273, 275	$C_{15}H_{12}ClNO_2$	65.44 (65.29	4.38 4.42	5.11 5.10)

Table IV. IR and NMR Data for 2-(2-Quinolyl)-1,3-cyclohexanediones (**11a—c**)

Compound No.	IR (cm^{-1}, Nujol) C=O	NH	NMR ($CDCl_3$, δ) C_4–H	C_3–H	Ar–H	NH[a]	CH_2
11a	1645	3120	8.08 (1H, d, J=10 Hz)	9.13 (1H, d J=10 Hz)	7.35—7.80 (4H, m)	18.0 (1H, br s)	1.99 (2H, quintet), 2.62 (4H, t)
11b	1625	3100		9.06 (1H, s)	7.40—7.92 (4H, m)	17.60 (1H, s)	2.00 (2H, quintet), 2.61 (4H, t)
11c	1625	3100		9.36 (1H, s)	7.40—7.80 (4H, m)	18.0 (1H, br s)	2.00 (2H, quintet), 2.61 (4H, t)

a) Each proton was exchangeable with deuterium oxide.

Taking account of the fact that the reaction of **1a** with 2,4-pentanedione in acetic anhydride gives 3-(2-quinolyl)-2,4-pentanedione only in a poor yield of 10%,[7] it is noticeable that the 1,3-cyclohexanedione system is much more reactive toward the nucleophilic reaction of aromatic *N*-oxide described here. However, *N*-ylide formation[1,4] was not observed at all, contrary to our expectation. The formation of **13** from the reaction of **7** with **10** is particularly significant in view of the inaccessibility of 4-substituted products in reactions of quinoline and pyridine 1-oxides with active methylenes in the presence of acetic anhydride. It seems likely that 3-(2,6-dioxocyclohexylidene)cyclohexanone was initially formed and then reacted with **7**, but the detailed features of the reaction remain to be explored.

Experimental

All melting points are uncorrected. IR spectra were recorded on a JASCO IR-E spectrometer. NMR spectra were measured with a JEOL PS-100 spectrometer at 100 MHz using TMS as an internal reference. Mass spectra were obtained on a JMS 01SG spectrometer.

Reactions of Quinoline 1-Oxides (1a—c) with Dimedone (2)——1) A solution of **1a—c** (5 mmol) in Ac_2O (5 ml) was added all at once to a solution of **2** (0.7 g, 5 mmol) in Ac_2O (5 ml) to give a yellow solution. The reaction mixture was heated at 90°C for 8 h, and then concentrated under reduced pressure. The residual solid mass was recrystallized from EtOH to give 5,5-dimethyl-2-(2-quinolyl)cyclohexane-1,3-diones, 4-(2-quinolyl)dimedones (**3a—c**).

2) A solution of **1a—c** (5 mmol) in DMF (4 ml) and Ac_2O (0.9 g, 7 mmol) was added to a solution of **2** (0.7 g, 5 mmol) in DMF (4 ml). The resulting yellow solution was heated at 90°C for 8 h, and processed as described above to give **3a—c**.

The results and some physical and spectral properties of the products are shown in Tables I and II.

Reactions of 3-Bromoquinoline 1-Oxide (1d) with 2——1) A solution of **1d** (1.12 g, 5 mmol) in Ac_2O (6 ml) was added all at once to a solution of **2** (0.7 g, 5 mmol) in Ac_2O (6 ml), and the resulting pale yellow solution was heated at 90°C for 8 h. The reaction mixture was concentrated under reduced pressure, and the residue was recrystallized from EtOH to give 1.68 g (87%) of 3-acetoxy-2-(3-bromo-2-quinolyl)-5,5-dimethyl-2-cyclohexenone (**3d'**), mp 145—146°C. *Anal.* Calcd for $C_{19}H_{18}BrNO_3$: C, 58.73; H, 4.64; N, 3.86. Found: C, 58.71; H, 4.71; N, 3.97. MS *m/e*: 387, 389 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 1665, 1770 (C=O). NMR ($CDCl_3$) δ: 1.24 (3H, s, CH_3–C(–)–CH_3), 1.32 (3H, s, CH_3–C(–)–CH_3), 1.88 (3H, s, CH_3–CO–), 2.53 (2H, s, $-CH_2$–CO–), 2.64 (1H, d, J=16 Hz, AcO–C(=)–C(H)–), 2.88 (1H, d, J=16 Hz, AcO–C(=)–C(H)–), 7.44—7.80 (3H, m, Ar–H), 8.08 (1H, dd, C_8–H of the quinoline ring), 8.37 (1H, s, C_4–H of the quinoline ring).

2) A solution of **1d** (1.12 g, 5 mmol) in DMF (6 ml) containing Ac_2O (0.9 g, 7 mmol) was added to a solution of **2** (0.7 g, 5 mmol) in DMF (6 ml) and the resulting pale yellow solution was heated at 90°C for 8 h to give 1.43 g (83%) of 4-(3-bromo-2-quinolyl)dimedone (**3d**) (Tables I and II).

Oxidation of 3a to Quinaldic Acid 1-Oxide (4)——A mixture of **3a** (0.267 g, 1 mmol), 30% H_2O_2 (20 ml) and AcOH (20 ml) was refluxed for 7 h to give an almost colorless solution. The solvent was removed under reduced pressure, H_2O (20 ml) was added, and the deposited crystals were recrystallized from MeOH to give 0.14 g of **4** (74%), pale brown needles, mp 169—170°C (dec.).

Reaction of Isoquinoline 2-Oxide (5) with 2——1) A solution of **5** (0.78 g, 5 mmol) in Ac_2O (6 ml) was added to a solution of **2** (0.7 g, 5 mmol) in Ac_2O (6 ml), and the resulting yellow solution was heated at 90°C for 8 h. The reaction mixture was concentrated under reduced pressure, and the residual solid mass was recrystallized from MeOH to give 1.3 g (100%) of 4-(1-isoquinolyl)dimedone (**6**), yellow needles, mp 199—201°C. *Anal.* Calcd for $C_{17}H_{17}NO_2$: C, 76.18; H, 6.41; N, 5.24. Found: C, 76.18; H, 6.48; N, 5.24. IR ν_{max}^{Nujol} cm^{-1}: 1650 (C=O), 3200 (NH). NMR ($CDCl_3$) δ: 1.20 (6H, s, 2×CH_3), 2.52 (4H, s, 2×CH_2), 7.22—7.80 (5H, m, Ar–H), 8.2 (1H, d, C_8–H of the isoquinoline ring), 11.70 (1H, br s, NH).

2) A solution of **5** (0.78 g, 5 mmol) in DMF (5 ml)–Ac_2O (0.9 g, 7 mmol) was added to a solution of **2** (0.7 g, 5 mmol), and the resulting yellow solution was heated at 90°C for 8 h to give 0.91 g (69%) of **6**.

Reaction of Pyridine 1-Oxide (7) with 2——1) A solution of **7** (0.38 g, 4 mmol) in Ac_2O (5 ml) was added all at once to a solution of **2** (0.56 g, 4 mmol) in Ac_2O (8 ml), and the whole was heated at 90°C for 8 h. The yellow reaction mixture was concentrated under reduced pressure, and the residue was recrystallized from MeOH to give 0.42 g (48%) of 4-(2-pyridyl)dimedone (**8**), pale yellow needles, mp 162—163°C. *Anal.* Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.69; N, 6.55. Found: C, 71.91; H, 7.01; N, 6.35. IR ν_{max}^{Nujol} cm^{-1}: 1635 (C=O). NMR ($CDCl_3$) δ: 1.09 (6H, s, 2×CH_3), 2.48 (4H, s, 2×CH_2), 7.0—8.0 (3H, m, Ar–H), 9.21 (1H, d, J=10 Hz, C_3–H of the pyridine ring).

2) A solution of **7** (0.38 g, 4 mmol) in DMF (5 ml)–Ac_2O (0.8 g, 6 mmol) was added to a solution of **2** (0.56 g, 4 mmol) in DMF (5 ml), and the resulting pale yellow solution was heated at 90°C for 8 h to give 0.4 g (45%) of **8**.

Oxidation of 8 to Picolinic Acid 1-Oxide (9)——A mixture of **8** (0.5 g), 30% H_2O_2 (20 ml) and AcOH (20 ml) was refluxed for 5 h to give an almost colorless solution. The solvent was removed under reduced pressure, and the residue was recrystallized from H_2O to give 0.16 g (56%) of **9**, colorless needles, mp 156—166°C (dec.). It was identified by direct comparison with an authentic sample [*cf.* lit.,[8] mp 166°C].

Reaction of Quinoline 1-Oxides (1a—c) with 1,3-Cyclohexanedione (10)——A solution of **1a—c** (5 mmol) in Ac_2O (5 ml) was added all at once to a solution of **10** (0.56 g, 5 mmol) in Ac_2O (5 ml). The resulting yellow solution was heated at 90°C for 8 h, and then concentrated under reduced pressure. The residual solid mass was recrystallized from EtOH to give the corresponding 2-substituted quinolines (**11a—c**).

The results and some physical and spectral data of **11a—c** are shown in Tables III and IV.

Oxidation of 11a to 4——A solution of **11a** (0.5 g) and 30% H_2O_2 (20 ml) in AcOH (20 ml) was refluxed for 7 h to give 0.27 g (74%) of **4**.

Reaction of 5 with 10——A solution of **5** (0.78 g, 5 mmol) in Ac_2O (5 ml) was added to a solution of **10** (0.56 g, 5 mmol) in Ac_2O (5 ml), and the resulting yellow solution was heated at 90°C for 8 h. The solvent was removed under reduced pressure, and the oily residue was triturated with MeOH to give a crystalline solid, which was recrystallized from MeOH to give 0.95 g (73%) of the 1-substituted isoquinoline (**12**), yellow prisms, mp 79°C. *Anal* Calcd for $C_{16}H_{16}NO_3$: C, 71.21; H, 5.91; N, 5.13. Found: C, 70.97; H, 6.33; N, 5.15. MS *m/e*: 271 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 1720 (C=O), 2400 (OH). NMR ($CDCl_3$) δ: 2.06 (2H, quintet, C_5–H_2 of the cyclohexanone ring), 2.42 (4H, t, C_4–H_2 and C_6–H_2 of the cyclohexanone ring), 3.65 (3H, s, OCH_3), 6.70 (1H, d, J=10 Hz, C_4–H of the isoquinoline ring), 7.20—8.02 (5H, m, Ar–H), 15.85 (1H, br s, OH).

Reaction of 7 with 10——1) A solution of **7** (0.38 g, 4 mmol) in Ac_2O (5 ml) was added all at once to a solution of **10** (0.45 g, 4 mmol) in Ac_2O (7 ml), and the resulting orange solution was heated at 90°C for 8 h. The reaction mixture was concentrated under reduced pressure, and the residue was recrystallized from EtOH–ether to give 0.41 g (39%) of the 4-substituted pyridine (**13**), orange needles, mp 269—270°C. *Anal.* Calcd for $C_{17}H_{17}NO_3$: C, 72.06; H, 6.05; N, 4.94. Found: C, 71.94; H, 6.03; N, 5.06. MS *m/e*: 283 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 2200—2400 (OH), 1640 (C=O). NMR ($CDCl_3$) δ: 1.48—2.90 (12H, m), 1.52 (1H, br s, OH), 7.83 (2H, d, J=8 Hz, C_3–H and C_5–H of the pyridine ring), 8.99 (2H, d, J=8 Hz, C_2–H and C_6–H of the pyridine ring).

2) A solution of **7** (0.38 g, 4 mmol) in DMF (5 ml)–Ac_2O (0.8 g, 6 mmol) was added all at once to a solution of **10** (0.45 g, 4 mmol) in DMF, and the resulting orange solution was heated at 90°C for 8 h to give 0.34 g (32%) of **13**.

Oxidation of 13 to Isonicotinic Acid 1-Oxide (14)——A mixture of **13** (0.283 g), 30% H_2O_2 (20 ml) and AcOH (20 ml) was refluxed for 7 h to give 0.084 g (61%) of **14**, colorless needles, mp 266°C [lit.,[9] mp 266°C].

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References and Notes

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