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Stable Sulfur Ylides. IV.*,[1] Reaction of Dimethylsulfonium Acetylmethoxycarbonylmethylide and Dimethylsulfonium Diacetylmethylide with Quinoline 1-Oxide

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Dimethylsulfonium acetylmethoxycarbonylmethylide (Ia) was found to react with quinoline 1-oxide (II) in the presence of benzoyl chloride to give three compounds: 1-methoxycarbonyl-2-oxo-3-(2-quinolyl)-1,2-dihydropyrrolo[1,2-*a*]quinoline (III), 1-methoxycarbonyl-2-oxo-1,3-di(2-quinolyl)-1,2-dihydropyrrolo[1,2-*a*]quinoline (IV), and 2-benzoyloxy-1-methoxycarbonyl-3-(2-quinolyl)pyrrolo[1,2-*a*]quinoline (V). Similarly, the reaction of dimethylsulfonium diacetylmethylide (Ib) with II gave 4-benzoyl-1-methyl-2-methylthio-3-oxo-3*H*-pyrido[1,2-*a*]quinoline (XII).

In our previous paper,[3] it was reported that dimethylsulfonium benzoylmethylide, which possessed one electron-withdrawing substituent at ylide carbon, reacted with quinoline 1-oxide in the presence of an acylating agent to afford dimethylsulfonium 2-quinolylbenzoylmethylide. A few reports have been published on the reaction of stable ylides which possessed two electron-withdrawing substituents at ylide carbon. Nozaki reported the reactions of dimethylsulfonium diacetylmethylide (Ib) with diethyl acetylenedicarboxylate[4] and diphenylcyclopropenone.[5]

In our present investigation, it was found that dimethylsulfonium acetylmethoxycarbonylmethylide (Ia) and Ib, which were more stable than dimethylsulfonium benzoylmethylide, reacted with quinoline 1-oxide (II) in the presence of an acylating agent to give interesting compounds.

Reaction of Ia with Quinoline 1-Oxide

When benzoyl chloride was added dropwise to an ice-cooled solution of dimethylsulfonium acetylmethoxycarbonylmethylide (Ia) and quinoline 1-oxide (II) in chloroform. An exothermic reaction occurred, and the solution turned rapidly to reddish brown. After treatment with alkaline, the reaction product was separated to three compounds by column chromatography on silica gel; the compound (III) of mp 217—219° as red fine crystals in 30.2% yield, the compound (IV) of mp 265—266° as reddish orange fine crystals in 14.1% yield, and the compound (V) of mp 224° as pale yellow needles in trace. The structures of these compounds were assigned as 1-methoxycarbonyl-2-oxo-3-(2-quinolyl)-1,2-dihydropyrrolo[1,2-*a*]quinoline (III), 1-methoxycarbonyl-1,3-di(2-quinolyl)-2-oxo-1,2-dihydropyrrolo[1,2-*a*]quinoline (IV), and 2-benzoyloxy-1-methoxycarbonyl-3-(2-quinolyl)-pyrrolo[1,2-*a*]quinoline (V), respectively, on the bases of the physical and chemical (Chart 1) data outlined below.

The infrared absorption (IR) spectra of III, IV, and V showed carbonyl absorption bands at 1742 and 1635 cm^{-1}, 1748 and 1659 cm^{-1}, and 1742 and 1695 cm^{-1}, respectively. The

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* Dedicated to the memory of Prof. Eiji Ochiai.

[1] Part III: M. Watanabe, T. Kinoshita, and S. Furukawa, *Chem. Pharm. Bull.* (Tokyo), **23**, 258 (1975).

[2] Location: *1-14 Bunkyo-machi, Nagasaki, 852, Japan.*

[3] S. Furukawa, T. Kinoshita, and M. Watanabe, *Yakugaku Zasshi*, **93**, 1064 (1973).

[4] Y. Hayashi, M. Kobayashi, and H. Nozaki, *Tetrahedron*, **26**, 4354 (1970).

[5] Y. Hayashi and H. Nozaki, *Tetrahedron*, **27**, 3085 (1971).

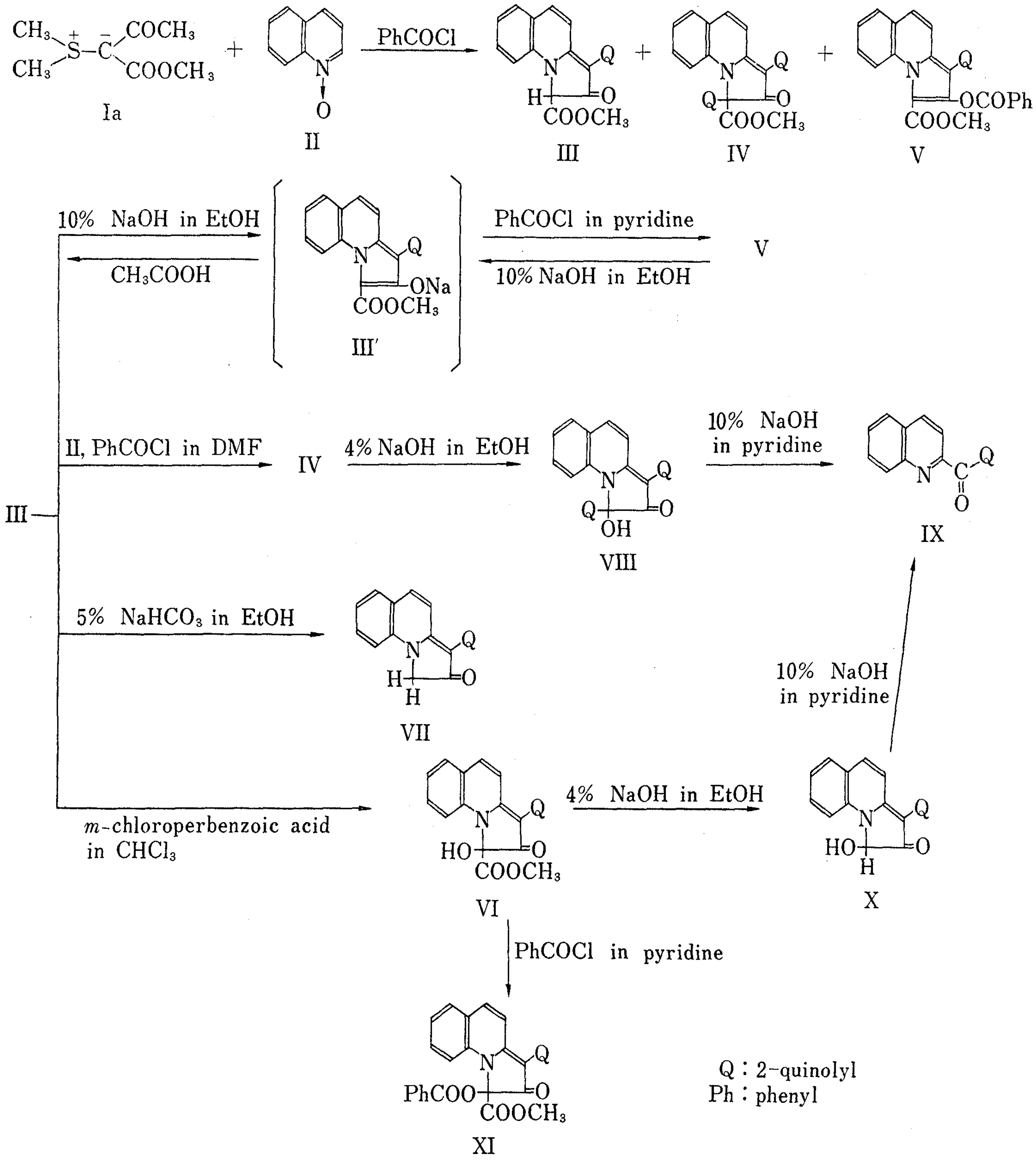

Chart 1

elemental analyses and the mass spectra of III, IV, and V were characterized as $C_{23}H_{16}O_3N_2$ (M^+, m/e 368), $C_{32}H_{20}O_3N_3$ (M^+, m/e 495), and $C_{30}H_{20}O_4N_2$ (M^+, m/e 472), respectively. The nuclear magnetic resonance (NMR) spectra of III, IV, and V revealed the absence of the signals attributable to the acetyl-hydrogens and dimethylsulfide-hydrogens.

The treatment of III with 10% sodium hydroxide in ethanol produced stable sodium salt (III') of mp>300° as yellow-green needles. III' was converted into V of mp 224° when treated with benzoyl chloride in pyridine, reversely the treatment of V with 10% sodium hydroxide in ethanol smoothly afforded III' and benzoic acid. III' was converted into III by the treatment of acetic acid in good yield. Moreover, the reaction of III with quinoline 1-oxide (II) in the presence of benzoyl chloride in N,N-dimethylformamide (DMF) gave IV of mp 265—266° in 53.1% yield. Also III was completely converted into VI of mp 234—236° as red needles when the chloroform solution of III was allowed to stand for 7 days at room temperature. Similarly, the conversion of III into VI proceeded rapidly in the presence of *m*-chloroperbenzoic acid in chloroform. The IR spectrum of VI showed carbonyl absorption bands at 1755 cm^{-1} and 1633 cm^{-1}, hydroxy absorption band at 3400 cm^{-1}. The elemental analysis and the mass spectrum of VI was characterized as $C_{23}H_{16}O_4N_2$ (M^+, *m/e* 384). According to these data, the structure of VI was assigned as 1-hydroxy-1-methoxycarbonyl-2-oxo-3-(2-quinolyl)-1,2-dihydropyrrolo[1,2-*a*]quinoline. From above results, it would assume that the formation of IV, V, and VI proceeded through III. III was treated with 5% sodium bicarbonate in ethanol for 3 hr under refluxing to form VII of mp 220—221° as dark red needles. The structure of VII was assigned as 2-oxo-3-(2-quinolyl)-1,2-dihydropyrrolo[1,2-*a*]quinoline, on the bases of the elemental analysis and spectral data of IR (ν_{CO} 1636 cm^{-1}) and mass. IV was refluxed with 4% sodium hydroxide in ethanol gave VIII of mp 253—254° as orange needles. The IR spectrum of VIII showed only absorption of hydroxy group at 3400 cm^{-1}, but no absorption at carbonyl region. By the treatment of VIII with 10% sodium hydroxide in pyridine at 80° for 4 hr, di-2-quinolyl ketone (IX) of mp 164—166° (mp 165—166°[6]) was obtained. According to above facts, the structure of VIII was assigned as 1-hydroxy-2-oxo-1,3-di(2-quinolyl)-1,2-dihydropyrrolo[1,2-*a*]quinoline. Then a solution of VI and 4% sodium hydroxide in ethanol was refluxed for 30 min to give X of mp 235° (decomp.) as dark red needles. The structure of X was assigned as 1-hydroxy-2-oxo-3-(2-quinolyl)-1,2-dihydropyrrolo[1,2-*a*]quinoline by the elemental analysis and mass spectrum (M^+, *m/e* 326). When a solution of X and 10% sodium hydroxide in pyridine was heated at 80°, di-2-quinolyl ketone (IX) was obtained in 80% yield.

VI was converted into the corresponding O-benzoyl compound (XI) of mp 243—244° as red needles when treated with benzoyl chloride in pyridine. The IR spectrum of XI showed carbonyl absorption bands at 1766, 1741, and 1660 cm^{-1}, but no hydroxy absorption band.

From these spectral and chemical data, it was assumed that intermolecular cyclization occurred between Ia and II, in which the bonds were formed between 2-position of quinoline and terminal methyl group of acetyl on Ia, and nitrogen of quinoline and ylide carbon accompanied with elimination of dimethyl sulfide of Ia. It was examined how the yield of reaction products would be affected by the nature of reaction medium or the amount of the reagents employed, and the results will be shown in Table I. From these results, it was found that the yields of products were affected to an amount of solvent. Namely the yields of III, IV, and

TABLE I. Reaction of Dimethylsulfonium Acetylmethoxycarbonylmethylide (Ia) with Quinoline 1-Oxide (II)

Number	Reaction					Products			
	Ia g (mole)	II g (mole)	PhCOCl g (mole)	Solvent (ml)	Time (hr)	III[a] g (%)	IV g (%)	V g (%)	Recovery of Ia g (%)
1	1.76 (0.01)	1.45 (0.01)	1.4 (0.01)	$CHCl_3$ 40	4	0.6 (16.3)	0.1 (2.0)	—	—
2	1.76	1.45	1.4	$CHCl_3$ 70	12	0.1 (2.7)	trace	—	1.2(68.2)
3	1.76	1.45	1.4	$CHCl_3$ 20	12	1.08 (29.3)	0.07 (1.4)	0.15 (3.2)	—
4	1.76	1.45	2.8 (0.02)	$CHCl_3$ 20	24	1.11 (30.2)	0.7 (14.1)	trace	—
5	1.76	1.45	1.4	CH_3CN 20	20	0.72 (19.6)	0.44 (8.9)	—	0.6(34.1)
6	1.76	1.45	1.4	DMF 4	12	0.95 (25.8)	0.69 (13.9)	—	—

a) small amount of VI contained as impurity

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6) M. Hamana and M. Yamazaki, *Chem. Pharm. Bull.* (Tokyo), **11**, 415 (1963).

V were decreased by using a large amount of reaction solvent, but the kinds of solvent in this reaction have little or not effect.

Reaction of Ib with Quinoline 1-Oxide

The reaction of dimethylsulfonium diacetylmethylide (Ib) with quinoline 1-oxide (II) in the presence of benzoyl chloride in DMF gave compound (XII) of mp 166—167° as pale orange plates in 26.5% yield, whose structure was assigned as 4-benzoyl-1-methyl-2-methylthio-3-oxo-3*H*-pyrido[1,2-*a*]quinoline on the bases of the physical and chemical (Chart 2) data outlined below.

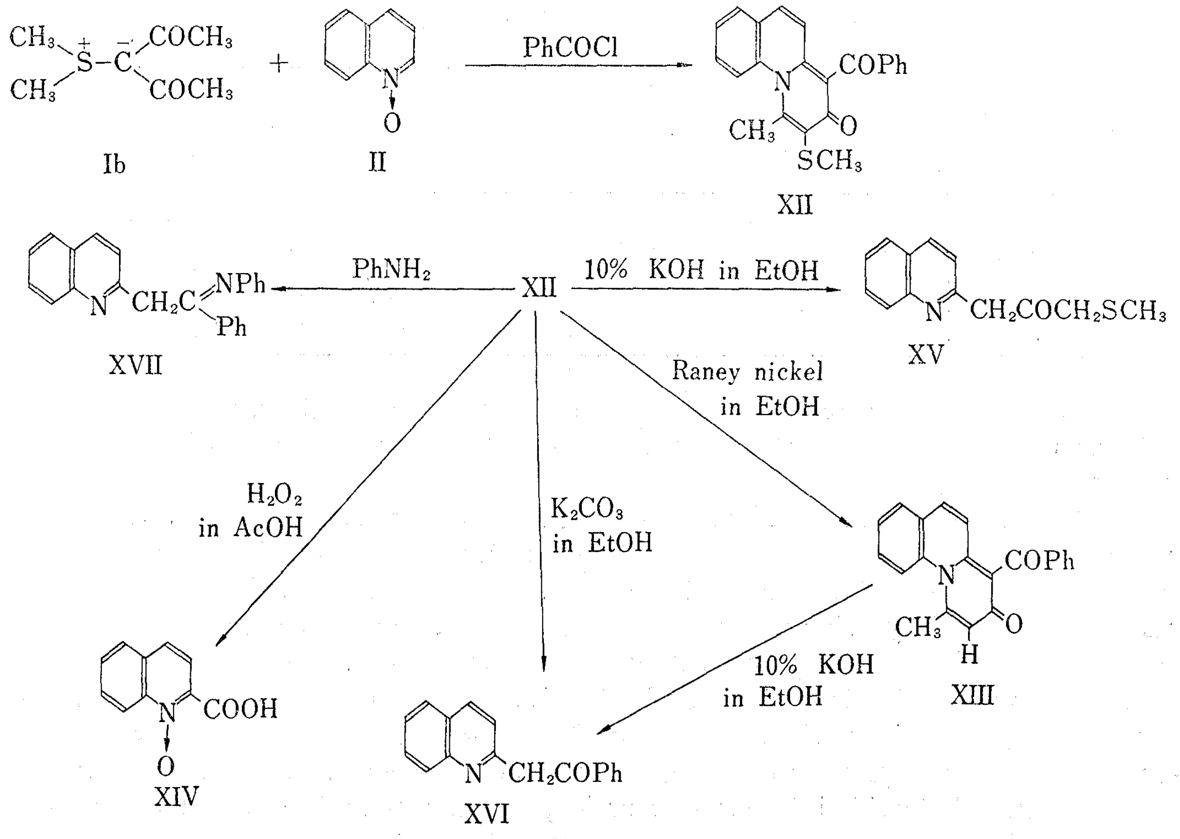

Chart 2

The elemental analysis and the mass spectrum of XII was consistent with $C_{22}H_{17}O_2NS$ (M^+, *m/e* 359). The NMR spectrum ($CDCl_3$) of XII showed signals at 2.42 ppm (methyl, singlet, 3H), 2.72 ppm (methylthio, singlet, 3H), and 7.24—8.28 ppm (aromatic, multiplet, 11H). The IR spectrum of XII showed carbonyl absorption band at 1623 cm^{-1}. The treatment of XII with 30% hydrogen peroxide in acetic acid in the usual method produced quinaldinic acid 1-oxide (XIV). A solution of XII in aniline was refluxed for 6 hr to give 2-phenacylquinoline anil[3] (XVII) of mp 160—161° as yellow needles. The Raney nickel desulfurization of XII in ethanol under refluxing gave XIII of mp 141° as light orange needles. The mass spectrum of XIII showed the expected molecular ion peak at *m/e* 313. The NMR spectrum ($CDCl_3$) of XIII showed signals at 2.34 ppm (methyl, singlet, 3H), 6.34 ppm (methine, singlet, 1H), and 7.18—8.17 ppm (aromatic, multiplet, 11H). The ultraviolet (UV) spectrum of XIII exhibited a quite similar absorption pattern to that of XII. According to above data, the structure of XIII was determined 4-benzoyl-1-methyl-3-oxo-3*H*-pyrido[1,2-*a*]quinoline. The treatment of XII with potassium carbonate in ethanol afforded 2-phenacylquinoline (XVI) of mp 118—119°, whose structure has been reported by Hamana[7] in detail. XVI was also prepared from XIII by treatment of 10% potassium hydroxide in ethanol under refluxing. On the other hand, refluxing the ethanol solution of XII and 10% potassium hydr-

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[7] M. Yamazaki, K. Noda, and M. Hamana, *Chem. Pharm. Bull.* (Tokyo), **18**, 908 (1970).

oxide gave 2-(3-methylthio)acetonylquinoline (XV) of mp 68—69° as yellow needles in 40% yield, whose structural assignment was based on its elemental analysis and spectral data of IR and NMR. The NMR spectrum ($CDCl_3$) of XV showed signals at 2.20 ppm (methylthio, singlet, 3H), 3.28 ppm (methyl, singlet, 3H), 5.56 ppm (methine, singlet, 1H), 6.64 ppm (3-position of quinoline, doublet $J=9$ Hz, 1H), and 7.24—7.69 ppm (aromatic, multiplet, 5H). From above facts, it was concluded that XV exists the enaminic form which has been described by Hamana.⁷⁾

Table II. Reaction of Dimethylsulfonium Diacetylmethylide (Ib) with Quinoline 1-Oxide (II)

Number	Reaction						Product	
	Ib g (mole)	II g (mole)	PhCOCl g (mole)	Solvent (ml)	Temperature	Time (hr)	XII g (%)	Recovery of Ib g (%)
1	3.2(0.02)	2.9 (0.02)	2.8(0.02)	$CHCl_3$ 25	reflux	2	1.4 (19.5)	—
2	1.6(0.01)	1.45(0.01)	1.4(0.01)	benzene 30	reflux	0.5	0.3 (8.4)	1.0(62.5)
3	3.2	2.9	2.8	CH_3CN 20	room temp.	2	trace	3.0(93.7)
4	1.6	1.45	1.4	DMF 8	room temp.	24	0.95(26.5)	—
5	3.2	2.9	5.6(0.04)	DMF 15	room temp.	24	1.9 (25.1)	—

Table II shows the reaction of Ib with II under various conditions, using of DMF as solvent seems to be more suitable than other solvents in the yield and isolation of XII as described experimental section.

In the reaction of Ia and quinoline 1-oxide, the several reaction products were obtained. In this reaction, although the molar ratio of ylide (Ia), quinoline 1-oxide, and acylating agent were changed, a sole product could not be obtain. In particular, the yields of reaction products were decreased by using a large amount of solvent. From the facts presented above, this reaction may be partially proceeded by the radical path way. But no effect was observed by the addition of perbenzoic acid or azobis-isobutyronitrile in this reaction mixture. When Ia or Ib was treated with pyridine 1-oxide or picoline 1-oxide in the same manner as quinoline 1-oxide, no reaction occurred and starting materials were recovered. Using of acetic anhydride instead of benzoyl chloride in the same reaction, the starting materials were also recovered. Although mechanism of this reaction has not been clarified yet, it was presumed from the structures of the reaction products that the terminal methyl group of acetyl on ylides reacted as nucleophile to quinoline 1-oxide in the presence of acylating agent. Further work is in progress on the reaction of these stable sulfur ylides with other aromatic amine N-oxides.

Experimental

All the melting points are uncorrected. NMR spectra were recorded on a JNM-PS-100 (JEOL) spectrometer using tetramethylsilane as an internal standard. Mass spectra were recorded on a JMS-01SG (JEOL) spectrometer. IR spectra were taken on an IRA-2 (JASCO) spectrophotometer. UV spectra were taken on an EPS-2 (Hitachi) spectrophotometer.

Reaction of Ia with II——To a solution of 1.7 g (0.01 mole) of Ia, 1.45 g (0.01 mole) of II, and 15 ml of $CHCl_3$, a solution of 2.8 g (0.02 mole) of benzoyl chloride and 5 ml of $CHCl_3$ was added dropwise with ice cooling and stirring. The resulting solution was allowed to stand at room temperature for 24 hr, the reaction mixture was condensed *in vacuo*. After addition of H_2O to the residue, the mixture made alkaline with 5% Na_2CO_3 and this was extracted with $CHCl_3$. After evaporation of $CHCl_3$ *in vacuo*, the red residue was dissolved in small amount of $CHCl_3$, and chromatographed over silica gel column. The first compound obtained from elution with $CHCl_3$ (0—200 ml) was recrystallized from AcOEt to give 0.05 g of V (pale yellow needles), mp 224°. *Anal.* Calcd. for $C_{30}H_{20}O_4N_2$: C, 76.26; H, 4.27; N, 5.93. Found: C, 76.06; H, 4.20; N, 5.77. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 236.5 (4.28), 270 (3.98), 290 (shoulder), 350 (3.77), 370 (shoulder), 384 (shoulder). NMR (TFAA⁸⁾) ppm: 4.02 (3H, singlet), 7.35—8.90 (17H, multiplet). The second compound obtained from elution

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8) Trifluoroacetic acid.

with $CHCl_3$ (200—400 ml) was recrystallized from $CHCl_3$ to give 0.7 g (14.1%) of IV (reddish orange fine crystals), mp 265—266°. *Anal.* Calcd. for $C_{32}H_{21}O_3N_3$: C, 77.56; H, 4.27; N, 8.48. Found: C, 77.67; H, 4.36; N, 8.50. UV λ_{max}^{EtOH} nm: 224, 281 (shoulder), 295, 350 (shoulder), 365, 478.[9] NMR (TFAA[8]) ppm: 3.83 (3H, singlet), 7.35—8.76 (18H, multiplet). The third compound obtained from elution with $CHCl_3$ (600—800 ml) was recrystallized from benzene to give 1.1 g (30.2%) of III (red fine crystals), mp 217—219°. *Anal.* Calcd. for $C_{23}H_{16}O_3N_2$: C, 74.99; H, 4.38; N, 7.61. Found: C, 74.95; H, 4.22; N, 7.44. UV λ_{max}^{EtOH} nm: 222, 284, 294 (shoulder), 350 (shoulder), 363, 392, 415, 480.[9] NMR (TFAA[8]) ppm: 4.04 (3H, singlet), 7.52—8.90 (12H, multiplet). The column eluted with CH_3CN gave 1.5 g of dark brown viscous oil. This oil could not be identified.

Conversion of III into V——A mixture of 0.3 g (0.8 mmole) of III, 1 ml of 10% NaOH, and 10 ml of EtOH was heated on a boiling water bath for 5 min. Immediately, the reaction mixture changed from red to yellow-green, and crystals separated. The crystals (III′) were collected and dried in a vacuum desiccator. To a solution of 0.25 g of III′ and 20 ml of pyridine, 1.5 ml of benzoyl chloride was added dropwise. The mixture was allowed to stand at room temperature for 24 hr. After evaporation of solvent, 10% NH_4OH was added to the residue, and crystals separated. The crystals were collected and recrystallized from AcOEt to give 0.15 g (40.6%) of V (pale yellow needles), mp 223°. This compound was identified with an authentic sample of V (mp 224°) obtained above reaction, by mixed melting point test and comparison of spectral data.

Conversion of V into III——A mixture of 0.3 g (0.6 mmole) of V, 1 ml of 10% NaOH, and 10 ml of EtOH was heated on a boiling water bath for 20 min. The separated yellow-green crystals (III′) was collected by filtration. The filtrate was concentrated, the residue was acidified with 10% HCl, and benzoic acid was obtained in quantitative yield. III′ was suspended in AcOH, crystals changed from yellow-green to red. The red crystals were collected and recrystallized from benzene to give 0.10 g (45.4%) of III, mp 217°. This compound was identified with an authentic sample of III (mp 217—219°) obtained previous reaction, by mixed melting point test and comparison of spectral data.

Conversion of III into IV——To a solution of 0.37 g (0.001 mole) of III, 0.14 g (0.001 mole) of II, and 20 ml of DMF, 0.14 g (0.001 mole) of benzoyl chloride was added dropwise at room temperature with stirring. The reaction mixture was concentrated *in vacuo*, 5% $NaHCO_3$ was added to the residue and this was extracted with $CHCl_3$. After evaporation of $CHCl_3$, the residue was recrystallized from $CHCl_3$ to give 0.26 g (53.1%) of IV, mp 265—266°. This compound was identified with an authentic sample of IV (mp 265—266°) obtained previous reaction, by mixed melting point test and comparison of spectral data.

Conversion of III into VI——a) A mixture of 0.05 g (0.13 mmole) of III, 0.05 g of *m*-chloroperbenzoic acid, and 10 ml of $CHCl_3$ was stirred at room temperature for 10 min. After evaporation of solvent, 5% Na_2CO_3 was added to the residue and this was extracted with $CHCl_3$. The extract was evaporated to dryness and the residue was recrystallized from benzene to give 0.04 g (80.0%) of VI (red needles), mp 234—236°. *Anal.* Calcd. for $C_{23}H_{16}O_4N_2$: C, 71.87; H, 4.20; N, 7.29. Found: C, 72.27; H, 4.13; N, 6.99. Mass Spectrum *m/e*: 384 (M^+). UV λ_{max}^{EtOH} nm (log ε): 223 (4.76), 281 (4.36), 300 (4.41), 350 (4.18), 364 (4.23), 495 (4.08). NMR (TFAA[8]) ppm: 3.88 (3H, singlet), 7.68—8.92 (13H, multiplet).

b) A solution of 0.05 g of III and 40 ml of $CHCl_3$ was allowed to stand at room temperature. After 7 days, VI was detected as one spot by thin-layer chromatography. The solution was evaporated to give VI.

Alkaline Decomposition of III——A solution of 0.5 g (0.13 mmole) of III, 20 ml of 5% $NaHCO_3$, and 40 ml of EtOH was refluxed for 3 hr. The reaction mixture was concentrated *in vacuo*, H_2O was added to the residue and this was extracted with $CHCl_3$. After evaporation of $CHCl_3$, the residue was recrystallized from benzene to give 0.02 g (50.0%) of VII (dark red needles), mp 220—221°. *Anal.* Calcd. for $C_{21}H_{14}ON_2$: C, 81.27; H, 4.55; N, 9.03. Found: C, 81.46; H, 4.60; N, 8.81. Mass Spectrum *m/e*: 310 (M^+). IR (KBr) cm^{-1}: 1636 ($\nu_{C=O}$). UV λ_{max}^{EtOH} nm: 218, 278 (shoulder), 292, 350 (shoulder), 365, 394, 417, 475.[9]

Alkaline Decomposition of IV——A mixture of 0.3 g (0.6 mmole) of IV, 5 ml of 4% NaOH, and 10 ml of EtOH was refluxed for 8 hr. After evaporation of solvent, the residue was washed with 10% AcOH. The separated crystals were collected and recrystallized from $CHCl_3$ to give 0.15 g (55.5%) of VIII (orange needles), mp 253—254°. *Anal.* Calcd. for $C_{30}H_{19}O_2N_2$: C, 79.45; H, 4.22; N, 9.27. Found: C, 79.27; H, 4.32; N, 9.27. Mass Spectrum *m/e*: 453 (M^+). UV λ_{max}^{EtOH} nm: 226, 283 (shoulder), 300, 356 (shoulder), 372, 488.[9] NMR (TFAA[8]) ppm: 7.44—9.13 (multiplet).

Alkaline Decomposition of VIII and X——A mixture of 0.3 g (0.7 mmole) of VIII, 5 ml of 10% NaOH, 10 ml of pyridine was heated at 100° for 3 hr. After evaporation of excess pyridine, H_2O was added to the residue and this was extracted with $CHCl_3$. The extract was evaporated to dryness, the residue was recrystallized from ether to give 0.1 g (50.0%) of IX, mp 164°. Similarly, when X was treated by the same manner described above, IX was obtained. *Anal.* Calcd. for $C_{19}H_{12}ON_2$: C, 80.26; H, 4.25; N, 9.85. Found: C, 80.02; H, 4.31; N, 9.42. IR (KBr) cm^{-1}: 1672 ($\nu_{C=O}$).

Alkaline Decomposition of VI——A mixture of 0.3 g (0.8 mmole) of VI, 5 ml of 4% NaOH, and 10 ml of EtOH was heated on a boiling water bath for 30 min. After evaporation of solvent, the residue was washed with 10% AcOH and H_2O. The separated crystals were collected and recrystallized from benzene–EtOH

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[9] Sparingly soluble (log ε could not be calculated).

to give 0.25 g (96.1%) of X (dark red needles), mp 235°. *Anal.* Calcd. for $C_{21}H_{14}O_2N_2$: C, 77.28; H, 4.32; N, 8.58. Found: C, 77.09; H, 4.32; N, 8.64. IR (KBr) cm^{-1}: 1695 ($\nu_{C=O}$), 3400 (ν_{OH}). UV λ_{max}^{EtOH} nm: 266 (shoulder), 283, 319, 354, 394 (shoulder), 460.[9]

Reaction of VI with Benzoyl Chloride——To a solution of 0.3 g (0.8 mmole) of VI and 10 ml of pyridine, 3 ml of benzoyl chloride was added at room temperature, the resulting solution was kept at room temperature for 2 hr. After evaporation of solvent, 5% $NaHCO_3$ was added to the residue and this was extracted with $CHCl_3$. The extract was condensed to dryness and the residue was recrystallized from AcOEt to give 0.26 g (66.6%) of XI (red needles), mp 243—244°. *Anal.* Calcd. for $C_{30}H_{20}O_5N_2$: C, 73.76; H, 4.13; N, 5.74. Found: C, 73.45; H, 3.96; N, 5.31. Mass Spectrum *m/e*: 488 (M$^+$). UV λ_{max}^{EtOH} nm (log ε): 225 (4.76), 285 (4.38), 301 (4.38), 350 (4.19), 363 (4.24), 500 (4.06). NMR ($CDCl_3$) ppm: 3.80 (3H, singlet), 7.44—9.35 (17H, multiplet).

Reaction of Ib with II——To a mixture of 1.6 g (0.01 mole) of Ib, 1.45 g (0.01 mole) of II, and 8 ml of DMF, 1.4 g (0.01 mole) of benzoyl chloride was added dropwise at room temperature with stirring. Gradually, the reaction mixture was changed from yellow to reddish brown. The reaction mixture was allowed to stand at room temperature for 24 hr, the resultant was poured into 60 ml of H_2O. This mixture made alkaline with 10% NaOH, and this was extracted with $CHCl_3$. After evaporation of $CHCl_3$ *in vacuo*, the residue was washed with a mixture of ether and petroleum ether. The separated crystalline mass was collected and recrystallized from AcOEt to give 0.95 g (26.5%) of XII (pale orange plates), mp 166—167°. *Anal.* Calcd. for $C_{22}H_{17}O_2NS$: C, 73.53; H, 4.77; N, 3.90; S, 8.90. Found: C, 73.46; H, 4.84; N, 3.82; S, 8.71. UV λ_{max}^{EtOH} nm (log ε): 233 (4.65), 320 (3.85). The washing solution was evaporated *in vacuo*, the residue was viscous oil of 1.3 g which could not be identified.

Reaction of XII with H_2O_2——A mixture of 0.36 g (0.001 mole) of XII, 1 ml of 30% H_2O_2, and 10 ml of AcOH was heated at 80° for 6 hr. The mixture was concentrated, ether was added to the residue, and the separated crystalline mass was collected. The crude product was recrystallized from benzene to give 0.12 g (63.1%) of quinaldinic acid 1-oxide (XIV), mp 167—168°.

Reaction of XII with Aniline——A solution of 0.36 g (0.001 mole) of XII and 10 ml of aniline was refluxed for 6 hr. After evaporation of aniline *in vacuo*, the residue was dissolved in benzene. The solution was chromatographed over a silica gel column, elution with benzene afforded the crystals which were recrystallized from ether to give 0.1 g (30%) of XVII (yellow needles), mp 160—161°. *Anal.* Calcd. for $C_{23}H_{18}N_2$: C, 85.68; H, 5.63; N, 8.69. Found: C, 86.08; H, 5.83; N, 8.54. Mass Spectrum *m/e*: 322 (M$^+$). IR (KBr) cm^{-1}: 1645 ($\nu_{C=N}$).

Desulfurization of XII——A mixture of 0.5 g (1.4 mmole) of XII, 9 g of Raney nickel (W-2), and 10 ml of EtOH was refluxed for 10 hr. The reaction mixture was filtered, and the filtrate was concentrated to dryness. The residue was dissolved in $CHCl_3$, and chromatographed over a silica gel column. The compound obtained from elution with $CHCl_3$–MeOH (10: 1) was recrystallized from ether to give 0.3 g (69.8%) of XIII (light orange needles), mp 141°. *Anal.* Calcd. for $C_{21}H_{15}O_2N$: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.85; H, 4.74; N, 4.23. IR (KBr) cm^{-1}: 1659 ($\nu_{C=O}$). UV λ_{max}^{EtOH} nm (log ε): 233.5 (4.66), 320 (3.77).

Alkaline Decomposition of XII——a) To a mixture of 0.6 g (1.6 mmole) of XII and 30 ml of EtOH, 1 g of K_2CO_3 and 2 ml of H_2O were added, the mixture was heated on a boiling water bath for 4 hr. The reaction mixture was concentrated *in vacuo*, H_2O was added to the residue and this was extracted with $CHCl_3$. After evaporation of $CHCl_3$, the residue was dissolved in ether. The solution was chromatographed over a silica gel column, elution with ether afforded the crystals which were recrystallized from hexane to give 0.25 g (64.1%) of XVI (yellow needles), mp 118—119°. *Anal.* Calcd. for $C_{17}H_{13}ON$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.51; H, 5.29; N, 5.37. IR (KBr) cm^{-1}: 1645 ($\nu_{C=O}$).

b) To a mixture of 0.8 g (2.2 mmole) of XII and 10 ml of EtOH, 2 ml of 10% KOH was added, and the mixture was heated at 80° for 5 hr with stirring, The reaction mixture was concentrated *in vacuo*, H_2O was added to the residue and this was extracted with $CHCl_3$. After evaporation of solvent, the residue was dissolved in ether, and chromatographed over a silica gel column. Elution with ether afforded the crystals which were recrystallized from hexane to give 0.2 g (40.0%) of XV (yellow needles), mp 68—69°. *Anal.* Calcd. for $C_{13}H_{13}ONS$: C, 67.52; H, 5.67; N, 6.06; S, 13.84. Found: C, 67.73; H, 5.48; N, 5.65; S, 13.71. IR (KBr) cm^{-1}: 1634 ($\nu_{C=O}$). UV λ_{max}^{EtOH} nm (log ε): 303 (4.10), 318 (4.03), 417 (4.20), 438 (4.05). Benzoic acid was obtained in quantitative yield from the aqueous layer.

Alkaline Decomposition of XIII——To a solution of 0.25 g (0.8 mmole) of XIII and 10 ml of EtOH, 1.5 ml of 10% KOH was added, and the mixture was heated at 80° for 5 hr. The reaction mixture was concentrated, H_2O was added to the residue and this was extracted with $CHCl_3$. After evaporation of $CHCl_3$, ether was added to the residue. The separated crystals were collected, and recrystallized from ether to give 0.05 g (25.0%) of XVI, mp 118°. This compound was identified with an authentic sample of 2-phenacylquinoline (XVI, mp 118—119°) obtained from previous reaction, by mixed melting point test and comparison of spectral data.

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