Studies on Tertiary Amine Oxides. XLVIII. The Reaction of Quinoline N-Oxide with Acrylonitrile

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Treatment of quinoline N-oxide (I) with acrylonitrile and acetic anhydride in hot dioxane or dimethylformamide resulted in the formation of β-(2-quinolyl)acrylonitrile (II) and di-(2-quinolyl)acetonitrile (III) in 34.4 and 3.3% yields, respectively. No definite product was obtained in the absence of acetic anhydride, whereas the reaction in excess acetic anhydride using no solvent caused the increase of the formation of III and conversely the decrease of that of II. In spite of such a markedly important role of acetic anhydride, it was further disclosed that, when a dioxane solution of I and acrylonitrile was heated in the presence of a catalytic amount of hydroquinone, II and β-(2-quinolyl)-lactonitrile (XI) were produced. The acrylonitrile derivative II should be assumed to result from the 1,3-dipolar cycloaddition between the free I and acrylonitrile. The mechanism of formation of III was also discussed. Acrylamide and ethyl acrylate showed similar behaviors to that of acrylonitrile.

Reactions of aromatic N-oxides of pyridine series with nucleophilic carbon compounds in the presence of acylating agents lead to the introduction of carbon-substituents into pyridine ring accompanied by deoxygenation of N-oxide function. All these reactions are rationalized as nucleophilic reactions of the initially formed acyl-adducts (A) of N-oxides, and α- or γ-substituted products are produced in most cases by the addition-elimination mechanism as illustrated by two representative examples in Chart 1. However significantly, the reaction of 4-quinolinol N-oxide with 1-morpholinocyclohexene in the presence of tosyl chloride affords a 3-substituted 4-quinolinol (D) by another path which involves the extrusion of tosylxy anion from 1-tosyloxy-4-quinolone (C) present in a small equilibrium concentration with 1-tosyloxy-4-quinolinol betaine (B) and concerted nucleophilic attack by the enamine at the electron-deficient 3-position as shown in Chart 1.

On the other hand in some cases, the 1,2-dihydro- and 1,4-dihydro-intermediates formed from acyl-adducts of aromatic N-oxides are known to undergo electrophilic substitution by means of enamine-like polarization followed by elimination of Acyl-X as shown in Chart 2. For example, quinoline N-oxide gives 3- and 6-nitro- and 3,6-dinitroquinoline N-oxides on treatment with acetyl chloride and silver nitrate in chloroform. Similar bromination with bromine and acetic anhydride are known with pyridine and quinoline N-oxides.

If an aromatic N-oxide could react with an electrophilic olefin such as acrylonitrile by this mechanism in the presence of an acylating agent, a β-substituted N-oxide might be formed

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by the electrophilic reaction of the Michael-type contrary to the nucleophilic one of 4-quinolinol N-oxide. In order to examine this possibility, acrylonitrile was applied to quinoline N-oxide in the presence of acetic anhydride. Although the object was not achieved, an unexpected and interesting reaction was encountered.

![Diagram of chemical reactions involving acrylonitrile and quinoline N-oxide](image)

**Chart 1**

**Chart 2**

E : NO₂, Br
A solution of quinoline N-oxide (I), 1 equivalent of acrylonitrile and 2 equivalents of acetic anhydride in dioxane or dimethylformamide was refluxed for 7—10 hours. Chromatographic separation of products on alumina gave a colorless crystalline compound (II), orange-red crystals (III) and carbostyril (IV) in 34.4, 3.3 and 8.4% yields, respectively.

The main product II had an empirical formula $C_{13}H_{14}N_2$ and was recrystallized from $n$-hexane as colorless needles, mp 116—118°. The infrared (IR) spectrum exhibited the characteristic nitrile band at 2220 cm$^{-1}$ and two bands indicative of a vinyl group at 1628 and 955 cm$^{-1}$. The nuclear magnetic resonance (NMR) spectrum showed no signal due to the $C_2$-H of quinoline ring.

Oxidation of II with 30% hydrogen peroxide in acetic acid afforded quinaldic acid N-oxide$^7$ (V), and II was hydrolyzed with sodium hydroxide in ethanol to $\beta$-(2-quinolyl)acrylic acid$^8$ (VI) which was in turn converted into the ethyl ester$^9$ (VII) by treatment with ethanol and phosphorus pentaoxide. The identity of VII was confirmed by direct comparison with an authentic sample prepared from VI obtained by the other known method$^8$ as shown in Chart 3.$^{10}$ Further, II itself was shown to be obtainable from the ester VII through the corresponding amide$^9$ (VIII), and conversely II was transformed into VIII with hydrogen peroxide and sodium hydroxide. Thus, II was determined unequivocally as $\beta$-(2-quinolyl)-acrylonitrile.

Recrystallization of III from benzene afforded red-orange needles of mp 281—283° (decomp.) with an empirical formula $C_{28}H_{23}N_3$. The IR spectrum displaced the nitrile band at 2170 cm$^{-1}$ and the NMR spectrum showed thirteen aromatic protons as a multiplet but any signals attributable to the $C_2$-H of quinoline ring were not observed. The compound III was also oxidized to IV$^7$ and was proved identical with an authentic sample of di-(2-quinolyl)-acetonitrile prepared from 2-chloroquinoline and acetonitrile.$^{11}$ From the NMR spectrum, its structure should be formulated as a structure containing intramolecular hydrogen bonding (III') as Scheibe and Daltrozzo have described.$^{12}$

These reactions are shown in Chart 3.

Apparently, the formation of II cannot be explained by the usual reaction course of an acyl-adduct of an aromatic N-oxide, and on the other hand one carbon atom has been removed during the formation of III. In exploring the essential feature and mechanism of this reaction examinations under various conditions were carried out, and the observations shown in Table I were obtained.

At first, it was revealed that the role of acetic anhydride was markedly important for the proceeding and the mode of reaction. Thus, when I was heated with acrylonitrile in dioxane or dimethylformamide or with an excess of acrylonitrile without acetic anhydride, the N-oxide I was recovered almost quantitatively and polymerization of acrylonitrile to various extent was observed. On the other hand, when I and acrylonitrile were heated in

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10. Since the acid VI melts at 193° accompanied by decomposition, its identification was performed as the ester VII which shows a clear melting point (69—71°).
excess acetic anhydride using no solvent, II was formed in a very small amount, conversely the yield of III increasing to 15.3%, and there was noticed the evolution of formaldehyde which was isolated as the dinedone adduct from the volatile gas generated from the reaction mixture. The use of benzoyl chloride or acetyl chloride instead of acetic anhydride in dioxane gave III as a sole product in a small yield of 3.4% in each case. No reaction was observed

![Chemical Reaction Diagram]

**Chart 3**

<table>
<thead>
<tr>
<th>Additive</th>
<th>Solvent</th>
<th>Reaction condition</th>
<th>Products (%)</th>
<th>Recovered I (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac₂O&lt;sup&gt;b&lt;/sup&gt;</td>
<td>dioxane</td>
<td>reflux 7 hr</td>
<td>II 34.4, III 3.3, IV 8.4</td>
<td>20</td>
</tr>
<tr>
<td>Ac₂O&lt;sup&gt;b&lt;/sup&gt;</td>
<td>DMF</td>
<td>reflux 7 hr</td>
<td>II 34.4, III 3.3, IV 8.4</td>
<td>20</td>
</tr>
<tr>
<td>Ac₂O&lt;sup&gt;b&lt;/sup&gt;</td>
<td>dioxane</td>
<td>room temperature 1 day</td>
<td>0.2, 4.5</td>
<td>89</td>
</tr>
<tr>
<td>Ac₂O</td>
<td>Ac₂O</td>
<td>reflux 7 hr</td>
<td>II 0.2, III 15.3, IV 10.6, IX&lt;sup&gt;a&lt;/sup&gt; 19.0</td>
<td>19</td>
</tr>
<tr>
<td>—</td>
<td>dioxane</td>
<td>reflux 7 hr</td>
<td>III —, IV —</td>
<td>trace 80&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>—</td>
<td>AN</td>
<td>reflux 7 hr</td>
<td>III —, IV —</td>
<td>— 90&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>PhCOCl&lt;sup&gt;b&lt;/sup&gt;</td>
<td>dioxane</td>
<td>reflux 7 hr</td>
<td>II 3.4, III 13.0, IV 3.9</td>
<td>39</td>
</tr>
<tr>
<td>AcCl&lt;sup&gt;b&lt;/sup&gt;</td>
<td>dioxane</td>
<td>reflux 7 hr</td>
<td>II 3.4, III 13.0, IV 1.7</td>
<td>20</td>
</tr>
<tr>
<td>TsCl&lt;sup&gt;b&lt;/sup&gt;</td>
<td>dioxane</td>
<td>reflux 7 hr</td>
<td>II trace, III trace</td>
<td>90</td>
</tr>
<tr>
<td>Base&lt;sup&gt;c&lt;/sup&gt;</td>
<td>dioxane</td>
<td>reflux 7 hr</td>
<td>II trace, III trace</td>
<td>90</td>
</tr>
</tbody>
</table>

<sup>a)</sup> IX: quinoline  
<sup>b)</sup> Two equivalents of the reagent were used.  
<sup>c)</sup> Polymerization of AN was markedly.  
<sup>d)</sup> Triton B, MeONa and NaH (in N₂)
in the presence of a base such as Triton B, sodium ethoxide and sodium hydride in place of acetic anhydride, only I being recovered.

Further, reactions with acrylamide and ethyl acrylate in the presence of acetic anhydride were found to give similar results. Whereas only ethyl β-(2-quinolyl)acrylate (VII) was formed in the latter case, the former reaction afforded not only acrylamide derivatives, VIII and its N-acetate (X), but also the acetonitrile compound III. The formation of III in this case may be associated with dehydration of the amide group by acetic anhydride during the reaction course (see Chart 4).

In spite of these observations, it was finally disclosed that I and acrylonitrile could enter into the reaction even in the absence of acetic anhydride when heated in dioxane in the presence of a catalytic amount of hydroquinone for 4 days, and II and the corresponding hydroxy derivative, β-(2-quinolyl)lactonitrile (XI) were formed, although in respective low yields. The dehydration of XI with acetic anhydride readily proceeded to give II. Reactions with acrylamide and the ethyl ester in the presence of hydroquinone also produced similar products; particularly noticeable is the sole formation of β-(2-quinolyl)lactamide (XII) in a good yield of 50% from the reaction of the amide (Chart 4).

\[ \begin{align*}
I + CH_2=CH-CN & \xrightarrow{\text{Ac}_2O, \text{heat}, \text{dioxane, 4 days}} \overset{\text{II}}{\text{II}} + \overset{\text{XI(3.5%)} \text{(3.3%)}}{\text{OH}} \\
I + CH_2=CH-CO\_2Et & \xrightarrow{\text{Ac}_2O, \text{heat}, \text{dioxane}} \overset{\text{XII(3.3%)}}{\text{XII(3.3%)}} \\
& \xrightarrow{\text{H.Q., dioxane}} \overset{\text{VII(50%)}}{\text{VII}} + \overset{\text{X(0.4%) \text{(14%)}}}{\text{X(0.4%)}} \\
& \xrightarrow{\text{H.Q., dioxane}} \overset{\text{VIII(3.5%) \text{(14%)}}}{\text{VIII}} + \overset{\text{X(0.4%) \text{(14%)}}}{\text{X(0.4%)}} \\
& \xrightarrow{\text{H.Q., dioxane}} \overset{\text{VII(50%)}}{\text{VII}} + \overset{\text{X(0.4%) \text{(14%)}}}{\text{X(0.4%)}} \\
& \xrightarrow{\text{H.Q., dioxane}} \overset{\text{VII(50%)}}{\text{VII}} + \overset{\text{X(0.4%) \text{(14%)}}}{\text{X(0.4%)}} \\
\end{align*} \]

From the above-mentioned results, the essential feature of the formation of the acrylonitrile II may most likely be the 1,3-dipolar cycloaddition between the free N-oxide I and acrylonitrile. The mode of the reaction agrees with those of cycloaddition of nitrones or some aromatic N-oxides and acrylic acid derivatives; the N-oxide function apparently behaves as an electron-releasing group. The low yields may possibly be ascribed to the rather large tendency of acrylonitrile towards polymerization.

In the reaction in the presence of hydroquinone, hydroquinone apparently acts as an inhibitor to the polymerization of acrylonitrile. In spite of the essential role of acetic anhydride, it should be considered that not the acetic anhydride-adduct of the N-oxide (XIV) but

the free N-oxide existing in equilibrium with XIV is the reactive species in the reaction using acetic anhydride. Although the promoting effect of acetic anhydride is not perfectly clear yet, it seems highly probable that acetic anhydride also plays an important role in hindering the polymerization of acrylonitrile in addition to a promoter of the conversion of the cyclic adduct (XV) into the 2-substituted quinoline XVI and II (course a in Chart 5).

As for the mechanism of the formation of III, its structure and the fact that it is never formed without an acylating agent indicate that the first step should be nucleophilic addition of the α-carbon of acrylonitrile to the 2-position of XIV giving XVII. The subsequent courses, involving the next elimination step giving XVIII or XIX and the introduction of a second quinoline ring, are not necessarily clear. In order to explain the formation of not formaldehyde diacetate but formaldehyde itself, the cycloaddition between XIX and a second mole of I and the breakdown of the cyclic intermediate (XX) thus formed into the product III and formaldehyde according to path b in Chart 5 seems to be attractive. However the direction of the cycloaddition between XIX and I is the reverse to that of I and acrylonitrile observed in the formation of II. The alternative course which involves the nucleophilic reaction of a second mole of I with XVIII or XIX and the breakdown of the intermediate (XXI) in a manner formulated in Chart 5 (course c) may be conceivable. Although 2-quinolylacetonitrile (XII) was found to react very readily with I in the presence of acetic anhydride even at room temperature to give III in quantitative yield, the intermediacy of XII seems to be improbable.

The reaction of pyridine N-oxide with acrylonitrile gave no definite product in spite of many attempts under similar conditions, polymers of acrylonitrile being produced accompanied

\[ \begin{align*}
\text{I} & \xrightarrow{\text{Ac}_2\text{O}} \text{XIV} \\
& \xrightarrow{\text{AcO}^- \text{OAc}} \text{XIV} \\
& \xrightarrow{\text{CH}_2=\text{CHCN}} \text{XVII} \\
& \xrightarrow{\text{CH}_2=\text{CHCN}} \text{XVIII} \\
& \xrightarrow{\text{CH}_2=\text{CHCN}} \text{XIX} \\
& \xrightarrow{\text{CH}_2=\text{CHCN}} \text{XXII} \\
& \xrightarrow{\text{CH}_2=\text{CHCN}} \text{III} \\
& \xrightarrow{\text{HOR}} \text{II} \\
& \xrightarrow{\text{HOR}} \text{XVI} \\
& \xrightarrow{\text{OR}} \text{XV} \\
& \xrightarrow{\text{OR}} \text{XVII} \\
& \xrightarrow{\text{OR}} \text{XVIII} \\
& \xrightarrow{\text{OR}} \text{XIX} \\
& \xrightarrow{\text{OR}} \text{XXI} \\
& \xrightarrow{\text{OR}} \text{XX} \\
\end{align*} \]

Chart 5

by the recovery of the N-oxide, and isoquinoline N-oxide seems to be much less reactive as compared with I towards the reaction concerned here.

Experimental

Reaction of Quinoline N-Oxide (I) with Acrylonitrile (AN) —— 1) A solution of I (1.45 g), Ac₂O (2.20 g) and AN (0.53 g) in dioxane (10 ml) was refluxed for 7—10 hr. The reaction mixture was evaporated under reduced pressure, made alkaline with saturated NaHCO₃ solution and extracted with CHCl₃. The benzene solution of extracted substances was passed through an alumina column. The first fraction gave 0.62 g of β-(2-quinolyl)acrylonitrile (II), colorless needles, mp 116—118° (n-hexane). It was proved identical with an authentic sample prepared from β-(2-quinolyl)acrylamide (VIII) as described below. Anal. Calcd. for C₁₅H₁₂N₂: C, 79.98; H, 4.48; N, 15.55. Found: C, 80.18; H, 4.34; N, 15.55. IR νmax cm⁻¹: 2225 (CN), 1628, 955 (C=N). NMR (CDCl₃): 1.67—2.66 (6H, m) 2.33 (1H, d, J = 16 Hz), 3.26 (1H, d, J = 16 Hz). Picrate: mp 200—202° (decomp.) (MeOH). The second fraction afforded 0.05 g of di-(2-quinolyl)acetanilide (III), orange-red needles, mp 281—283° (decomp.) (benzene), which was identical with an authentic sample obtained from 2-chloroquinoline and acetonitrile. Anal. Calcd. for C₂₉H₂₃N₃: C, 81.36; H, 4.41; N, 14.24. Found: C, 81.12; H, 4.42; N, 14.42. IR νmax cm⁻¹: 2170 (CN). NMR (CDCl₃): 2.00—2.60 (13H, m). Further, 0.12 g of carboxystyril (IV), mp 196—198°, and 0.23 g of I were obtained from the succeeding eluate.

2) Other reactions listed in Table I were carried out and worked up in the same manner.

Reactions of β-(2-Quinolyl)acrylonitrile (II) —— 1) Oxidation: To a solution of II (1.5 g) in AcOH (10 ml) was added 30% H₂O₂ (10 ml), and the whole was heated on a water-bath for 10 hr and evaporated in vacuo to give 0.30 g of quinolinic acid N-oxide (V), colorless needles, mp 164—166° (decomp.) (EtOH—H₂O).

2) Hydrolysis: A solution of II (1.0 g), EtOH (40 ml) and 10% NaOH (40 ml) was refluxed for 1 hr, concentrated and extracted with CHCl₃ to remove the unchanged II. The residual solution was acidified with AcOH to pH 4.6 to deposit colorless crystals which were filtered and recrystallized from EtOH—H₂O to afford 1.05 g of β-(2-quinolyl)acrylic acid (VI), colorless needles, mp 201—203° (decomp.). Anal. Calcd. for C₁₄H₁₁O₃N: C, 67.62; H, 4.45; N, 7.07. Found: C, 67.58; H, 4.53; N, 7.30.

3) Conversion to the Amid VIII: To a stirring solution of II (0.1 g) in acetone (10 ml) was successively added dropwise 3% H₂O₂ (3 ml) and 3% NaOH (3 ml), and the whole was warmed at 40—50°. After 0.5 hr, an additional 3% H₂O₂ (3 ml) was added and the mixture was kept overnight at room temperature. Acetone was removed under reduced pressure and the residual solution was extracted with CHCl₃. The extract residue was washed with benzene and recrystallized from AcOEt to give 0.06 g of β-(2-quinolyl)acrylamide (VIII), colorless needles, mp 177—178°. Anal. Calcd. for C₁₃H₁₂O₂N₂: C, 72.73; H, 5.86; N, 14.14. Found: C, 72.59; H, 5.69; N, 14.12. Picrate: yellow needles, mp 204—205° (decomp.) (EtOH).

Ethyl β-(2-Quinolyl)acrylate (VII) —— A mixture of VI (0.4 g), P₂O₅ (0.6 g) and anhyd. EtOH (20 ml) was refluxed for 3 hr. The reaction mixture was evaporated, made alkaline with K₂CO₃ solution and extracted with ether. The ether was passed through an alumina column to give 0.40 g of ethyl β-(2-quinolyl)-acrylate (VII), colorless needles, mp 69—71° (n-hexane). Anal. Calcd. for C₁₄H₁₅O₂N: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.70; H, 5.90; N, 5.96. Picrate: yellow needles, mp 194—196° (decomp.) (MeOH). It was proved identical with a sample prepared in the same way from the acid VI which was obtained by hydrolysis of the condensation product of quinoline and chloral.

β-(2-Quinolyl)acrylamide (VIII) —— 1) Preparation from the Ester VII: A mixture of VII (0.1 g), 28% NH₂OH (1.5 g) and EtOH (5 ml) was stirred at room temperature for 3 days. After removal of the solvent, the residue was extracted with CHCl₃ to give 0.03 g of VIII, mp 177—178° (AcOEt).

2) Conversion to the Nitrile II: A solution of VIII (0.1 g) and Ac₂O (1 ml) in dioxane was refluxed for 8 hr. The reaction mixture was concentrated, treated with NaHCO₃ solution and extracted with CHCl₃. The extract residue was purified by chromatography over alumina with ether to give 0.02 g of II, mp 116—118° (n-hexane).

Di-(2-quinolyl)acetanitride (III) —— 1) Oxidation: Oxidation of III (0.10 g) with 30% H₂O₂ (2 ml) and Ac₂O (20 ml) afforded 0.02 g of V in the same way as that of II.

2) Synthesis from 2-Quinolylacetanitride (XXII): When XXII (1.68 g) was added to a mixture of I (1.45 g) and Ac₂O (10 ml), a reaction immediately ensued and orange-red crystals of III precipitated from the reaction mixture. The yield was almost quantitative.

Reaction of I with AN in the Presence of Hydroquinone (H.Q.) —— 1) Reaction: A solution of I (1.45 g), AN (0.53 g) and a catalytic amount of H.Q. (below 50 mg) in dioxane (10 ml) was heated at 100° for 4 days. The reaction mixture was evaporated in vacuo, and the basic fraction extracted with CHCl₃ was chromatogrammed.

— 1) All melting points are uncorrected. NMR spectra were measured with JNM-3H-60 spectrometers at 60 MC using tetramethyl silane as internal reference.
graphed over alumina with petr. ether and ether. The fraction eluted with petr. ether–ether (1:1) was recrystallized from n-hexane to give 0.06 g of II. The ether effluent was recrystallized from n-hexane to afford 0.67 g of β-(2-quinolyl)lactonitrile (XI), pale yellow needles, mp 115.5—117°C. *Anal.* Calcd. for C_{12}H_{13}N_{2}O_{3}: C, 72.73; H, 5.56; N, 14.14. Found: C, 72.48; H, 5.32; N, 14.90. IR ν_{max} cm^{-1}: 3080 (OH), 2120 (CN). NMR τ (CDCl_{3}) 1.62—2.65 (7H, m), 4.85 (1H, t, J=9.5 Hz), 6.50 (2H m). Picrate: yellow needles, mp 164—165°C (EtOH).

2) Dehydration of XI: A solution of XI (0.1 g) and Ac_{2}O (1 ml) in dioxane (5 ml) was refluxed for 7 h to give II in an almost quantitative yield.

**Reactions of I with Acrylamide**—1) Reaction in the Presence of Ac_{2}O: A solution of I (1.45 g), Ac_{2}O (2.20 g) and acrylamide (0.71 g) in dioxane (10 ml) was refluxed for 7 h. The reaction mixture was evaporated in vacuo, made alkaline with NaHCO_{3} solution and extracted with CHCl_{3}. The extracted substances were chromatographed on alumina with ether and MeOH. The first fraction eluted with ether afforded 0.006 g of III. The second one was recrystallized from EtOH to give 0.009 g of N-acetyl-β-(2-quinolyl)-acrylamide (X), colorless needles, mp 190—192°C. *Anal.* Calcd. for C_{12}H_{13}N_{2}O_{3}: C, 70.00; H, 5.00; N, 11.67. Found: C, 69.57; H, 4.94; N, 11.50. IR ν_{max} cm^{-1}: 3130 (NH), 1730, 1685 (C=O), 1645, 975 (C=C). NMR τ (CD_{3}COOH): 0.26 (1H, s), 1.57—1.90 (8H, m), 2.47 (3H, s). It was proved identical with an authentic sample prepared by acetylation of VIII. The MeOH effluent was recrystallized from AcOEt to give 0.28 g of VII, colorless needles, mp 177—178°C.

2) Reaction in the Presence of H.O.: A solution of I (1.45 g), acrylamide (0.71 g) and a catalytic amount of H.O. in dioxane (10 ml) was heated at 100°C for 4 days. The resultant precipitates were recrystallized from EtOH to give 1.20 g of β-(2-quinolyl)lactamide (XII), colorless needles, mp 173—174°C. *Anal.* Calcd. for C_{13}H_{14}O_{2}N_{2}: C, 64.58; H, 6.87; N, 10.69. Found: C, 64.35; H, 6.56; N, 11.01. IR ν_{max} cm^{-1}: 3340 (OH), 3160, 3040 (NH), 1645 (C=O). NMR τ (CD_{3}COOH): 1.60—2.30 (9H, m), 4.90 (1H, t, J=9 Hz), 6.10 (2H, m). Picrate: yellow needles, mp 192—193°C (decomp.) (MeOH). *Anal.* Calcd. for C_{14}H_{15}O_{2}N_{2}: C, 58.43; H, 3.37; N, 15.74. Found: C, 48.33; H, 3.43; N, 15.97.

3) Dehydration of XII: A solution of XII (0.1 g) and Ac_{2}O (1 ml) in dioxane (5 ml) was refluxed for 7 h to give X, mp 190—192°C, in an almost quantitative yield.

**Reactions of I with Ethyl Acrylate**—1) Reaction in the Presence of Ac_{2}O: A solution of I (1.45 g), Ac_{2}O (2.20 g) and ethyl acrylate (1.0 g) in dioxane (10 ml) was refluxed for 7 h, and the reaction mixture was worked up in the similar way as the reaction with acrylamide. The fraction eluted with petr. ether–ether (1:1) from an alumina column was recrystallized from n-hexane to give 0.115 g of VII, colorless needles, mp 69—71°C.

2) Reaction in the Presence of H.O.: A solution of I (1.45 g), ethyl acrylate and a catalytic amount of H.O. in dioxane (10 ml) was heated at 100°C for 4 days. The reaction mixture was evaporated, and the basic fraction extracted with CHCl_{3} was chromatographed over alumina with petr. ether and ether. The petr. ether–ether (1:1) effluent was recrystallized from n-hexane to afford 0.08 g of ethyl β-(2-quinolyl)-lactate (XIII), colorless scales, mp 108—109.5°C. *Anal.* Calcd. for C_{14}H_{15}O_{2}N: C, 68.57; H, 6.12; N, 5.71. Found: C, 68.57; H, 6.23; N, 5.70. IR ν_{max} cm^{-1}: 3050 (OH), 1735 (C=O). NMR τ (CDCl_{3}): 1.83—2.79 (7H, m), 5.23 (1H, t, J=10 Hz), 5.75 (2H, q, J=14 Hz), 6.53 (2H, m), 8.75 (3H, t, J=14 Hz).

3) Dehydration of XIII: A solution of XIII (0.1 g) and Ac_{2}O (1 ml) in dioxane (5 ml) was refluxed for 7 h to give VII in an almost quantitative yield.