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Studies on Tertiary Amine Oxides. LVII.[1] Re-examination of the Reaction of Quinoline 1-Oxide with Acetic Anhydride, and the Related Reactions

Kazuhisa Funakoshi,[2] Yoshiyuki Kuchino,[2a] Hiromichi Shigyo,[2b] Hirotsune Sonoda,[2c] and Masatomo Hamana[2]

Faculty of Pharmaceutical Sciences, Kyushu University[2]

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Detailed examination of the reaction of quinoline 1-oxide (**1**) with methacrylonitrile in the presence of acetic anhydride and the re-examination of the reaction of **1** with acetic anhydride have revealed that there is another reaction sequence leading to polyquinolylmethanes, [tri-(2-quinolyl)methane (**5**), N-(2-quinolyl)-2-(2-quinolylmethylene)-1,2-dihydroquinoline (**11**) and N-(2-quinolyl)-2-[di-(2-quinolyl)methylene]-1,2-dihydroquinoline (**6**)], besides the formation of carbostyril in the latter reaction.

Reactions of **1** with acetic anhydride in the presence of quinaldine, di-(2-quinolyl)-methane (**9**), cyanoacetic acid, malonic acid and phenylacetic acid were also examined in connection with the exploration of the mechanism of the above reaction, and the possible mechanism has been proposed.

It has been previously reported that 1,3-dipolar cycloaddition between quinoline 1-oxide and acrylic acid derivatives occurrs in the presence of acetic anhydride or hydroquinone to give 2-substituted quinolines through primary cycloadducts.[3] Whereas quinoline 1-oxide similarly reacted with methacrylonitrile in the presence of hydroquinone producing cyanohydrin of 2-acetonylquinoline or 2-acetonylquinoline and 2-cyanoquinoline, the reaction in the presence of acetic anhydride afforded a few kinds of polyquinolylmethanes besides 2-cyanoquinoline and carbostyril.[4] This paper deals with detailed examination of this reaction and the observations obtained from related reactions.

A solution of quinoline 1-oxide (**1**), methacrylonitrile and excess acetic anhydride in dioxane was refluxed for 8 hours. Chromatographic separation of products on alumina gave 2-cyanoquinoline (**2**), carbostyril (**3**), quinoline (**4**) and two crystalline products (**5** and **6**) in respectively small yields (Chart 1).

Product **5** was recrystallized from ethanol as thin pink needles of mp 194—195° with the empirical formula $C_{28}H_{19}N_3$, and was proved identical with an authentic sample of tri-(2-quinolyl)methane prepared from 2-chloroquinoline and quinaldine.[5] Oxidation of **5** with 30% hydrogen peroxide in hot acetic acid gave **3** and quinaldic acid 1-oxide (**7**),[6] and mild oxidation with 3% hydrogen peroxide in acetic acid yielded tri-(2-quinolyl)carbinol (**8**).[5] It was further found that **5** was convertible into product **6** on treatment with **1** and acetic anhydride (Chart 2).

Product **6** was recrystallized from benzene-ethanol as colorless needles, mp 334—335°, which exhibited no absorption band due to any functional group in the infrared (IR) spectrum

1) Part LVI: S. Saeki, A. Yamashita, Y. Morinaka, and M. Hamana, *Yakugaku Zasshi*, **96**, 456 (1976).
2) Location: *Maidashi, Higashi-ku, Fukuoka*; *a*) Present address: *Biology Division, National Cancer Center Research Institute, Tsukiji 5-chome, Chuo-ku, Tokyo*; *b*) Present address: *Kowa Chemical Lab., Noguchi-machi, Higashimurayama, Tokyo*; *c*) Present address: *Sato Pharm. Co., Higashiohi, Shinagawa-ku, Tokyo.*
3) M. Hamana, K. Funakoshi, and Y. Kuchino, *Chem. Pharm. Bull.* (Tokyo), **22**, 1806 (1974).
4) M. Hamana, K. Funakoshi, H. Shigyo, and Y. Kuchino, *Chem. Pharm. Bull.* (Tokyo), **23**, 346 (1975).
5) G. Scheibe and E. Rossner, *Ber.*, **53B**, 2064 (1920).
6) Y. Hamada, *Yakugaku Zasshi*, **79**, 908 (1959).

and showed only signals resulting from aromatic protons in its nuclear magnetic resonance (NMR) spectrum. The elemental analysis and mass spectrum (M^+, *m/e* 524) accorded with the molecular formula $C_{37}H_{24}N_4$.

Oxidative cleavage of **6** by means of 30% hydrogen peroxide in hot acetic acid gave **3** and **7** similarly to that of **5**, and treatment with 5% hydrogen peroxide in hot acetic acid afforded **3** and **8**. While **6** dissolved in diluted mineral acid to give deeply red-violet solution, it underwent hydrolysis on heating with 60% sulfuric acid or 35% hydrochloric acid to give di(2-quinolyl)methane (**9**)[7] and N-(2-quinolyl)carbostyril (**10**)[8] (Chart 2). The identities of **7**, **8**, **9** and **10** were established by direct comparison with the respective authentic samples prepared by the known methods. On the basis of these observations, N-(2-quinolyl)-2-[di-(2-quinolyl)methylene]-1,2-dihydroquinoline was assigned to **6**.

When reactions of **1** with methacrylonitrile and acetic anhydride were carried out otherwise without solvent, triquinolylcarbinol **8** was also obtained as the third polyquinolylmethane, although the detailed features of reactions were somewhat different from each other (Chart 1).

Early in 1948, Ochiai and Okamoto[9] have carried out the reaction of **1** with acetic anhydride under reflux and isolated two colored by-products and quinoline in addition to a small

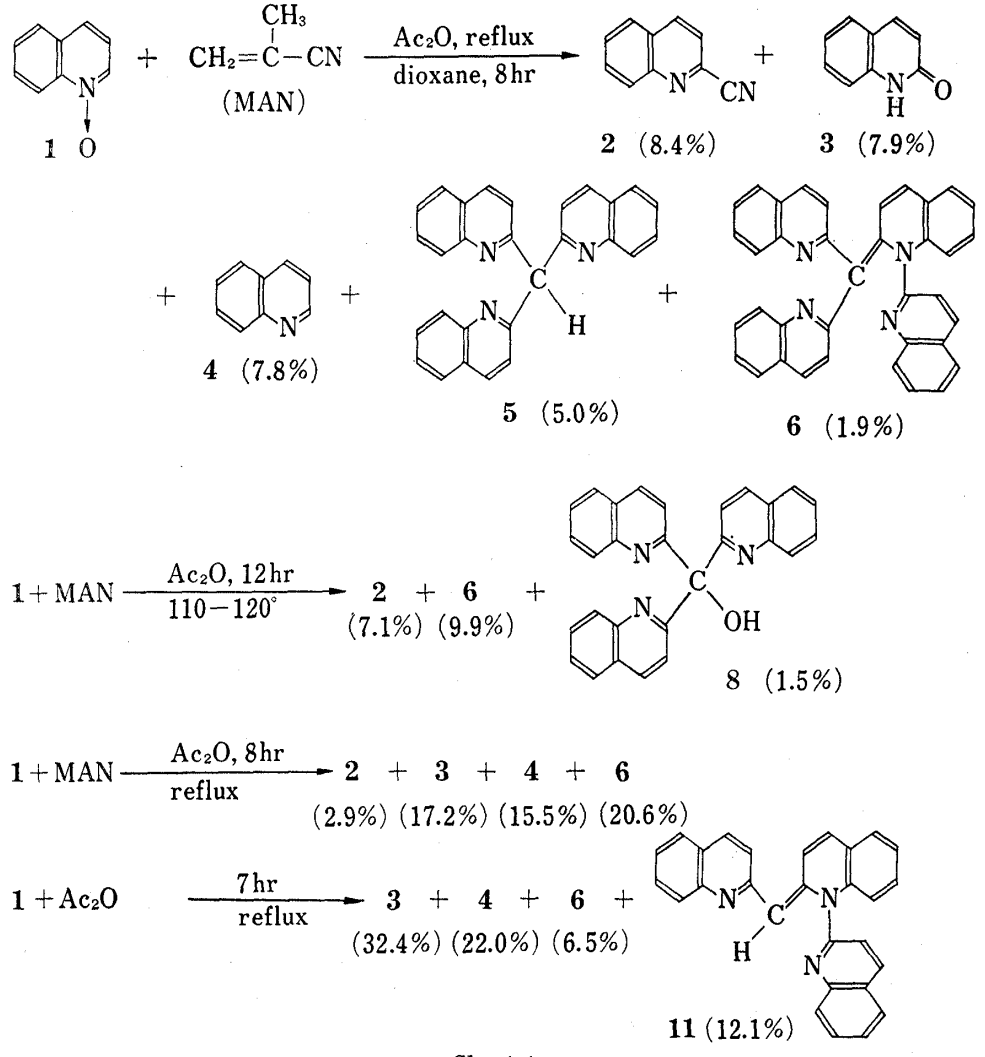

Chart 1

7) G. Scheibe and H.J. Friedrich, *Ber.*, **94**, 1336 (1961).
8) *a*) M. Murakami and E. Matsumura, *Nippon Kagaku Zasshi*, **72**, 509 (1951); *b*) K. Takeda and K. Hamamura, *Yakugaku Zasshi*, **73**, 1158 (1953).
9) E. Ochiai and T. Okamoto, *Yakugaku Zasshi*, **68**, 88 (1948).

amount of expected carbostyril **3** (20—35%), but their structures have not been elucidated. Considering that the central carbon-atom of the above-mentioned polyquinolylmethanes (**5**, **6** and **8**) might originate from the methyl group of acetic anhydride, we re-examined in detail the reaction of **1** with acetic anhydride under the same condition, and obtained **3**, **4**, **6** and a new triquinolyl compound (**11**), yellow prisms, mp 253—254°, in 32.4, 22.0, 6.5 and 12.1% yields, respectively (Chart 1).

Product **11** showed blue fluorescence[9] when dissolved in organic solvents, and its IR spectrum exhibited no absorption band ascribed to any functional group and the NMR spectrum showed signals only in the aromatic region. The analytical values and the mass spectrum (M^+, *m/e* 397) agreeded with the same molecular formula $C_{28}H_{19}N_3$ as that of **5**.

Oxidation of **11** with 30% hydrogen peroxide in hot acetic acid afforded **3** and **7** in the same way with the cases of **5** and **6**, but was not hydrolyzed with 60% sulfuric acid or 35% hydrochloric acid and no carbinol formation was noticed on treatment with diluted hydrogen peroxide in acetic acid. Differently from compound **5**, transformation of **11** into tetraquinolyl compound **6** by heating with **1** and acetic anhydride failed, no definite product being isolated. Although data supporting the structure of **11** are not necessarily enough, **11** may be likely assigned N-(2-quinolyl)-2-(2-quinolylmethylene)-1,2-dihydroquinoline on the basis of the above-mentioned observations as well as the related reactions described below.

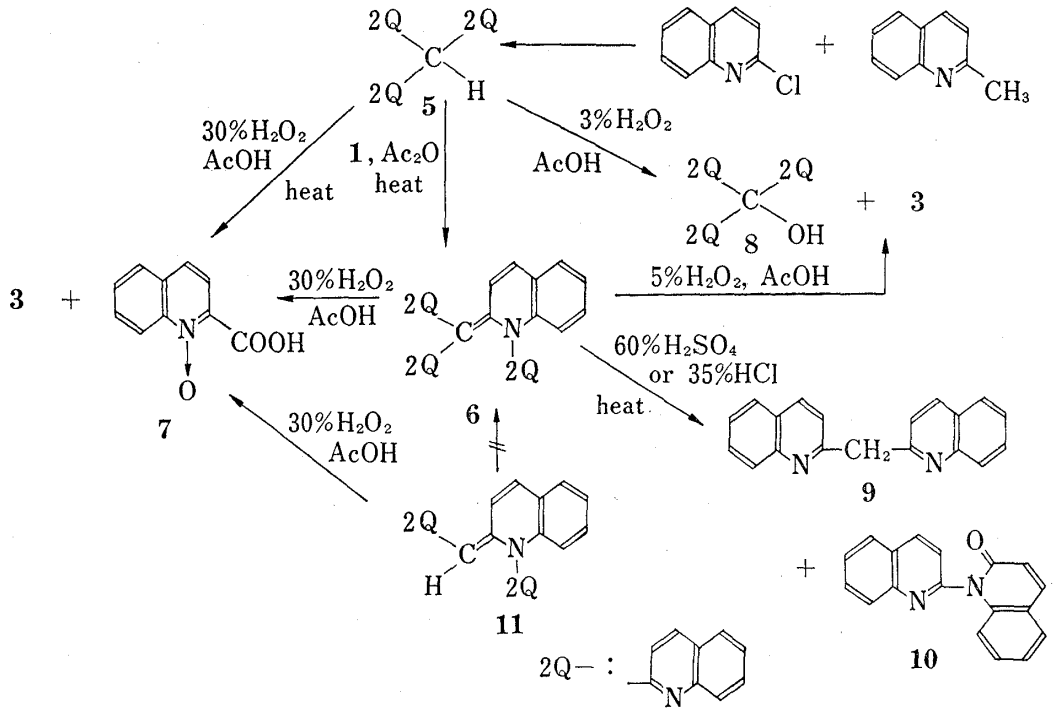

Chart 2

Thus it was disclosed that the formation of polyquinolylmethanes, **5**, **6**, **8** and **11**, results from the direct reaction of **1** with acetic anhydride, although 1,3-dipolar cycloaddition also occurrs to a small extent in the presence of methacrylonitrile giving **2**. In these reactions, the participation of the methyl group of acetic anhydride as nucleophile and decarboxylation of some intermediate during the reaction course are most likely essential for the smooth proceeding. In exploring these aspects we first examined reactions of quinaldine and di-(2-quinolyl)-methane **9** with **1** and acetic anhydride, and then those of some carboxylic acids susceptible to decarboxylation with the same reagents.

The reaction of quinaldine with **1** and acetic anhydride under reflux resulted in the formation of tetraquinolylmethane **6** and triquinolylmethane **11** in moderate yields. The total

yield of the products was found to be higher in the reaction applying somewhat excess of **1** than in that using equivalent of **1**, and **6** was always predominant. Treatment of **9** with about 2.5 equivalents of **1** in acetic anhydride under reflux afforded **3**, tetraquinolylmethane **6**, two triquinolyl compounds **8** and **11**, and di-(2-quinolyl) ketone (**12**)[10] in 19.2, 27.3, 4.3, 13.5 and 8.4% yields, respectively (Chart 3).

As for carboxylic acid, cyanoacetic acid, malonic acid and phenylacetic acid were applied. The reaction of **1** with cyanoacetic acid in acetic anhydride at room temperature gave di-(2-quinolyl)acetonitrile (**13**)[3] as the sole product in 46.3% yield, neither triquinolyl nor tetraquinolyl compounds being detected. However, the reaction with malonic acid under the same condition afforded polyquinolylmethanes **5** and **6** in 8.3 and 18.2% yields, respectively. Further, it was interestingly found that the reaction with phenylacetic acid under refluxing condition produced phenyl-di-(2-quinolyl)carbinol (**15**), mp 176—177°, and N-(2-quinolyl)-2-(phenyl-2-quinolylmethylene)-1,2-dihydroquinoline (**16**), mp 200—202°, in respective yields of 10.4 and 1.4%, in addition to 2-benzylquinoline (**14**, 6.0%), **3** (0.7%) and **4** (3.4%). The identity of **14** was confirmed by direct comparison with an authentic sample prepared from **1** and benzylmagnesium bromide.[11] Apparently, **15** and **16** are monophenyl analogues of **8** and **6**, and their structure assignment was based on their analytical values and the spectroscopic examinations as well as the mechanistic viewpoints (Chart 3).

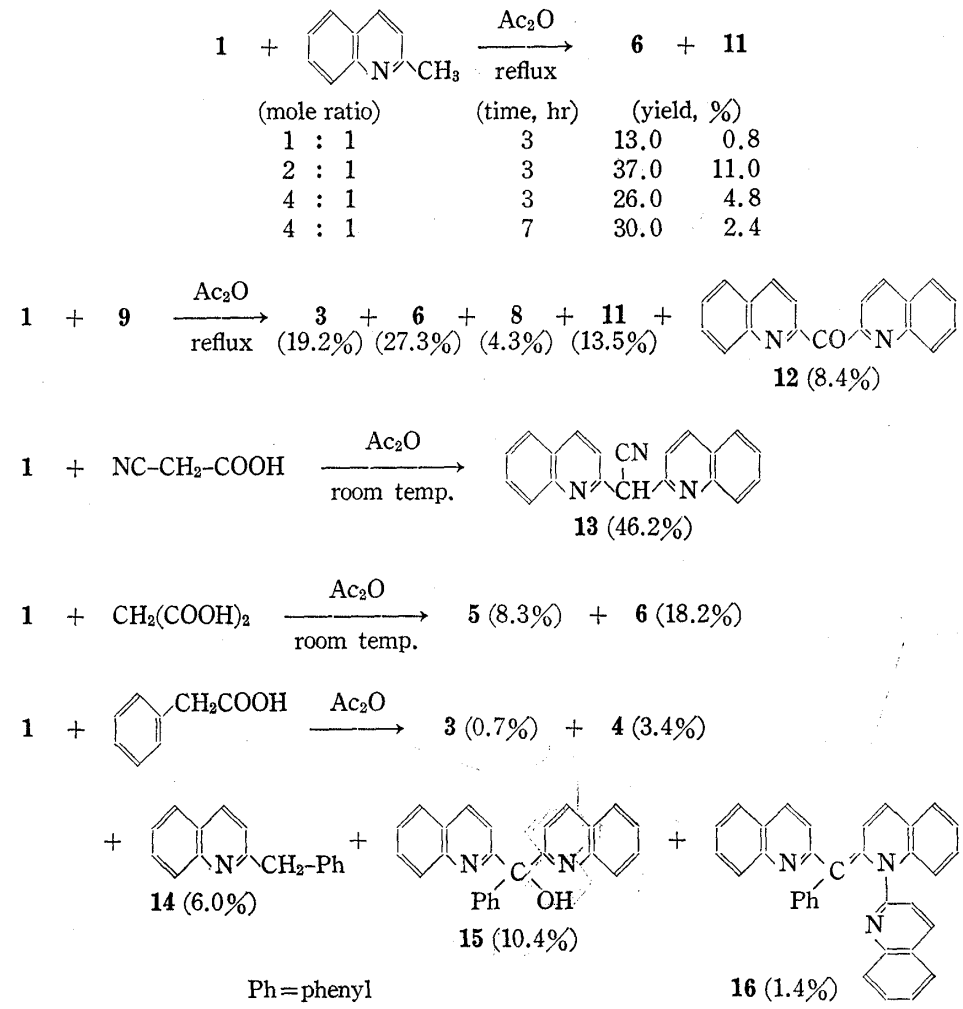

Chart 3

10) G. Scheibe and G. Schmidt, *Ber.*, **55**, 3157 (1922).
11) T. Kato, H. Yamanaka, and M. Hikichi, *Yakugaku Zasshi*, **85**, 331 (1965).

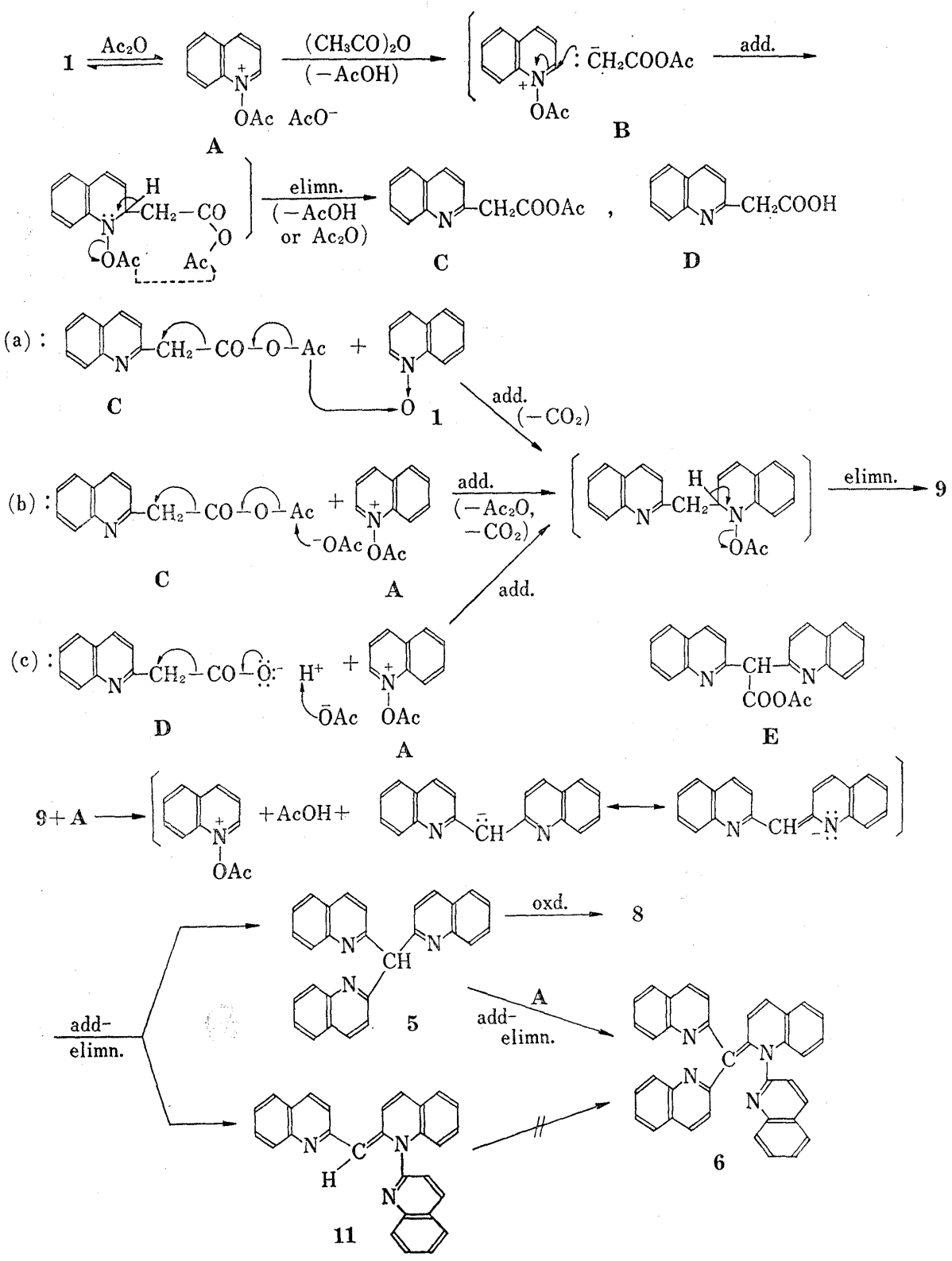

Chart 4

Although the details of the mechanism of the formation of polyquinolylmethanes, **5**, **6**, **8** and **11**, have not been established, all these products may be reasonably rationalized by the intermediacy of di-(2-quinolyl)methane **9** (Chart 4). Apparently the first step is the nucleophilic reaction of the initially formed N-acetoxyquinolinium acetate (**A**) with the carbanion (**B**) produced from acetic anhydride by means of the acetate anion of **A**. While this is essentially the same type as the reaction of **A** with active methylenes,[12] the nature of 2-substituted quinoline thus formed (**C** or **D**) and the details of their conversion to **9** by the consecutive reaction with the second molecule of **1** or **A** are not necessarily clear. As for the formation of 9 from **C** or **D**, it may be tentatively conceivable three courses [(a), (b) and (c)] involving nucleophilic attack of the 2-quinolylmethyl anion at the cation of **A** concerted with decarboxylation. The plausibility of course (a) or (b) may be clarified by studying the reaction of appropriate mixed anhydrides with **1** or **A**. Although **D** is well known to be highly susceptible to decarboxylation giving quinaldine,[13] it seems more probable that **D** reacts with another molecule of **A** by course (c) immediately after it formed; a stepwise path through quinaldine is apparently not proper.

The possibility of the formation of an anhydride (**E**) from **A** and **C** is not completely excluded, but only the successive transformation of **9** into polyquinolylmethanes will be discussed here.

The methylene group of **9** is highly active and the subsequent nucleophilic attack of **9** at another A molecule may readily occur by paths involving the carbanion or the nitrogen anion as the active center, leading to **5** or **11**, respectively. The easy oxidation of **5** probably during work-up affords carbinol **8**. As for the formation of tetraquinolyl compound **6**, the path from **5** is obviously correct and the alternative one from **11** should be ruled out from the attempted reactions of **1** with **5** or **11** in the presence of acetic anhydride (Chart 4).

All the results obtained from reactions carried out in the presence of quinaldine, di-(2-quinolyl)methane **9**, malonic acid and phenylacetic acid apparently support the above interpretation on the reaction course. Especially the last reaction is much significant for further development of similar type of nucleophilic reaction of aromatic N-oxide. However, the fact[14] that the reaction of pyridine 1-oxide with acetic anhydride gives 2-pyridone as the sole product in a high yield seemingly indicates that the naphthoidal reactivity of the ring is essential for the initiation of this type of reaction.

Recently, Yamanaka, *et al.* have described that 1-(1,2-dihydro-2-acetylisoquinolyl)acetic acid is formed when isoquinoline is heated with acetic anhydride.[15] Apparently the crucial step of this reaction is essentially the same with that of the formation of polyquinolylmethanes reported here.

Experimental[16]

Reaction of Quinoline 1-Oxide (1) with Methacrylonitrile in the Presence of Acetic Anhydride——1) A solution of **1** (2.9 g), methacrylonitrile (1.4 g) and Ac_2O (10 ml) in dioxane (10 ml) was refluxed for 8 hr. The reaction mixture was evaporated *in vacuo*, made alkaline with $NaHCO_3$ solution and extracted with $CHCl_3$. The extracted products were chromatographed on alumina. Elution with CCl_4 gave 0.005 g (1.9%) of N-(2-quinolyl)-2-[di-(2-quinolyl)]methylene-1,2-dihydroquinoline (**6**), colorless needles, mp 334—335° (benzene–EtOH). *Anal.* Calcd. for $C_{37}H_{24}N_4$: C, 84.71; H, 4.61; N, 10.68. Found: C, 84.88; H, 4.62; N, 10.64. NMR τ ($CDCl_3$): 1.80—2.77. Mass Spectrum *m/e*: 524 (M^+). Elution with benzene afforded successively 0.26 g (8.4%) of 2-cyanoquinoline (**2**), mp 94—95°, and 0.2 g (7.8%) of quinoline (**4**). The first fraction eluted with ether was recrystallized from EtOH to give 0.12 g (5.0%) of tri-(2-quinolyl)methane (**5**), thin pink needles,

12) M. Hamana and M. Yamazaki, *Chem. Pharm. Bull.* (Tokyo), **11**, 415 (1963).
13) W. Borsche and R. Manteuffel, *Ann.*, **526**, 22 (1936).
14) M. Katada, *Yakugaku Zasshi*, **67**, 51 (1947).
15) H. Yamanaka, T. Shiraishi, and T. Sakamoto, *Heterocycles*, **3**, 1080 (1975).
16) All melting and boiling points are uncorrected. NMR spectra were measured with JNM-3H-60 spectrometers at 60MC using tetramethyl silane (TMS) as internal reference.

mp 194—195°. *Anal.* Calcd. for $C_{28}H_{19}N_3$: C, 84.63; H, 4.79; N, 10.58. Found: C, 84.71; H, 4.73; N, 10.65. It was proved identical with an authentic sample prepared from 2-chloroquinoline and quinaldine.[5] Further, second and third fractions afforded 0.23 g (7.9%) of carbostyril (**3**), colorless needles, mp 197—199°, and 0.42 g of **1**, respectively.

2) A solution of **1** (1.45 g) and methacrylonitrile (0.7 g) in Ac_2O (10 ml) was heated at 110—130° (bath temp.) for 12 hr. Similar processing gave 0.13 g (9.9%) of **6**, 0.11 g (7.1%) of **2** and 0.02 g (1.5%) of tri-(2-quinolyl)carbinol (**8**), colorless prisms, mp 165—167°. Product **8** was isolated from ether eluate of alumina column, and identified by direct comparison with a sample obtained by H_2O_2-oxidation of **5** (see below).

3) Another run using **1** (1.45 g), methacrylonitrile (1.23 g) and Ac_2O (15 ml) under reflux for 8 hr afforded 0.27 g (20.6%) of **6**, 0.045 g (2.9%) of **2**, 0.25 g (17.2%) of **3** and 0.2 g (15.5%) of **4**.

Reactions of 5——1) Oxidation with 30% H_2O_2–AcOH: A mixture of **5** (0.2 g), 30% H_2O_2 (1 ml) and AcOH (2 ml) was heated on a water bath for 5 hr. The reaction mixture was evaporated *in vacuo*, made alkaline with $NaHCO_3$ solution and extracted with $CHCl_3$ to give 0.06 g (41.4%) of **3**, mp 198—199° (MeOH). The residual solution was acidified with AcOH to pH 4.6 and extracted with $CHCl_3$ to give 0.03 g (31.7%) of quinaldic acid 1-oxide (**7**),[6] colorless needles, mp 164—166° (decomp.) (EtOH–H_2O).

2) Oxidation with 3% H_2O_2–AcOH: A solution of **5** (0.397 g) and 3% H_2O_2 (3 ml) in AcOH (5 ml) was warmed at 60° on a water bath for 0.5 hr. The reaction mixture was evaporated, made alkaline with Na_2CO_3 solution and extracted with $CHCl_3$. The extracted substances were chromatographed on alumina with AcOEt to give 0.27 g (65.4%) of **8**,[5] colorless prisms, mp 165—167° (ether). *Anal.* Calcd. for $C_{28}H_{19}ON_3$: C, 81.33; H, 4.63; N, 10.16. Found: C, 81.51; H, 4.85; N, 10.31. IR ν_{max}^{Nujol} cm^{-1}: 3150 and 1072 (OH).

3) Reaction with **1** and Ac_2O: A solution of **5** (0.199 g) and **1** (0.08 g) in Ac_2O (2 ml) was refluxed for 2 hr. The reaction mixture was evaporated *in vacuo*, made alkaline with Na_2CO_3 solution and extracted with $CHCl_3$. The extracted substances were chromatographed on alumina with ether gave 0.13 g (49.2%) of **6**, colorless needles, mp 333—335° (MeOH).

Reactions of 6——1) Oxidation with 30% H_2O_2–AcOH: A mixture of **6** (0.5 g), 30% H_2O_2 (2 ml) and AcOH (5 ml) was heated on a water bath for 10 hr, and the reactants were treated similarly to the case of **5** to give 0.21 g (50.6%) of **3** and 0.13 g (68.8%) of **7**.

2) Oxidation with 5% H_2O_2–AcOH: A mixture of **6** (0.3 g), 5% H_2O_2 (3 ml) and AcOH (10 ml) was heated on a water bath for 3 hr. The reaction mixture was evaporated *in vacuo*, made alkaline with saturated $NaHCO_3$ solution and extracted with $CHCl_3$. The extract was evaporated and taken up in AcOEt. The AcOEt solution was passed through a silica gel column to give 0.05 g (60.3%) of **3** and 0.12 g (50.8%) of **8**. It was proved identical with a sample obtained by H_2O_2–oxidation of **5**.

3) Hydrolysis with 60% H_2SO_4: A solution of **6** (0.5 g) in 60% H_2SO_4 (20 ml) was refluxed for 5 hr. The reaction mixture was carefully made alkaline with saturated Na_2CO_3 solution and extracted with $CHCl_3$. The $CHCl_3$ extract was washed with 10% HCl to remove the basic fraction and then evaporated to give 0.21 g (81.1%) of N-(2-quinolyl)-2-quinolone (**10**),[8] colorless prisms, mp 170—172° (MeOH). The basic fraction gave 0.18 g (70.0%) of di-(2-quinolyl)methane (**9**),[7] light brown needles, mp 106—107° (petr. ether–ether).

4) Hydrolysis with 35% HCl: A solution of **6** (0.5 g) in 35% HCl (20 ml) was refluxed for 5 hr and processed in the same way to give 0.15 g (58.4%) of **10** and 0.21 g (81.1%) of **9**.

Reaction of 1 with Acetic Anhydride——A solution of **1** (1.45 g) in Ac_2O (10 ml) was refluxed for 7 hr. Excess Ac_2O was evaporated *in vacuo*, and the residue was made alkaline with saturated $NaHCO_3$ solution and extracted with $CHCl_3$. The extracted substances were chromatographed on an alumina column with ether and MeOH. Ether elution of the column gave three fractions. The first gave 0.32 g (22.0%) of **4**. The second one afforded 0.085 g (6.5%) of **6**, colorless needles, mp 331—333° (benzene–EtOH). The last effluent was recrystallized from ether to give 0.16 g (12.1%) of N-(2-quinolyl)-2-(2-quinolylmethylene)-1,2-dihydroquinoline (**11**), pale yellow prisms, mp 253—254°. *Anal.* Calcd. for $C_{28}H_{19}N_3$: C, 84.63; H, 4.79; N, 10.58. Found: C, 84.53; H, 4.68; N, 10.68. NMR τ (CF_3COOH): 1.15—2.40 (m). Mass Spectrum *m/e*: 397 (M^+).

Oxidation of 11 with 30% H_2O_2–AcOH——A mixture of **11** (0.5 g), 30% H_2O_2 (2 ml) and AcOH (5 ml) was heated on a water bath for 10 hr, and processed in the same way as the case of **5** to give 0.1 g (27.4%) of **3** and 0.11 g (46.2%) of **7**.

Reaction of Quinaldine with 1 and Acetic Anhydride——1) A solution of **1** (1.45 g) and quinaldine (1.43 g) in Ac_2O (10 ml) was refluxed for 3 hr. Excess Ac_2O was evaporated *in vacuo*, made alkaline with saturated $NaHCO_3$ solution and extracted with $CHCl_3$. The extracted substances were chromatographed on alumina. The fraction eluted with CCl_4 gave 0.17 g (13.0%) of **6**, colorless needles, mp 334—335° (benzene–EtOH). The ether eluate afforded 0.01 g (0.8%) of **11**, pale yellow prisms, mp 254° (ether). Further, a trace of carbostyril **3** was detected in the MeOH eluate.

2) Other runs using 2 and 4 equivalents of **1** under the similar conditions gave the results shown in Chart 2.

Reaction of 9 with 1 and Acetic Anhydride——A solution of **1** (0.73 g) and **9** (0.52 g) in Ac_2O (10 ml) was refluxed for 8 hr. The reaction mixture was evaporated *in vacuo*, made alkaline with Na_2CO_3 solution and extracted with $CHCl_3$. The extracted substances were chromatographed on silica gel column using CCl_4, CH_2Cl_2 and AcOEt as eluent. Elution with CCl_4 gave 0.18 g (27.3%) of **6**. The next fraction eluted with

CCl_4-CH_2Cl_2 (1: 1) afforded 0.06 g (8.4%) of di-(2-quinolyl) ketone (**12**), colorless prisms, mp 163—165° (EtOH), which was proved identical with an authentic sample.[10] Further elution with CH_2Cl_2 gave 0.03 g (4.3%) of **8**, and that with AcOEt afforded successively 0.09 g (13.5%) of **11**, 0.14 g (19.2%) and 0.05 g of **1**.

Reaction of Cyanoacetic Acid with 1 and Acetic Anhydride——A solution of **1** (1.45 g) and cyanoacetic acid (1.0 g) in Ac_2O (10 ml) was stirred at room temperature for 15 hr. The reaction mixture was evaporated *in vacuo*, made alkaline with Na_2CO_3 solution and extracted with $CHCl_3$. The extract was passed through an alumina column to give 0.7 g (46.3%) of di-(2-quinolyl)acetonitrile (**13**),[3] orange-red needles, mp 281—283° (decomp.) (benzene).

Reaction of Malonic Acid with 1 and Acetic Anhydride——To a solution of **1** (1.45 g) in Ac_2O (10 ml) was added malonic acid (0.96 g) under cooling, and then the mixture was stirred at room temperature for 15 hr. The reaction mixture was evaporated *in vacuo*, made alkaline with Na_2CO_3 solution and extracted with $CHCl_3$. The extracted substances were chromatographed on silica gel. The fraction eluted with CCl_4 gave 0.25 g (18.2%) of **6**, mp 333—334°, and the CH_2Cl_2 effluent was recrystallized from EtOH to afford 0.11 g (8.3%) of **5**.

Reaction of Phenylacetic Acid with 1 and Acetic Anhydride——A solution of **1** (1.45 g) and phenylacetic acid (1.63 g) in Ac_2O (6 ml) was refluxed for 3 hr. The reaction mixture was evaporated *in vacuo*, made alkaline with Na_2CO_3 solution and extracted with $CHCl_3$. The extracted products were chromatographed on alumina using petr. ether, benzene, ether and MeOH as eluent. The first fraction eluted with petr. ether was recrystallized from acetone to give 0.022 g (1.4%) of N-(2-quinolyl)-2-(phenyl-2-quinolylmethylene)-1,2-dihydroquinoline (**16**), colorless needles, mp 200—202°. *Anal.* Calcd. for $C_{34}H_{23}N_3$: C, 86.23; H, 4.90; N, 8.87. Found: C, 86.20; H, 4.80; N, 8.96. NMR τ ($CDCl_3$): 1.9—2.8 (m). Mass Spectrum *m/e*: 473 (M^+). The second fraction afforded 0.13 g (6.0%) of 2-benzylquinoline (**14**), bp 156°. Its picrate, mp 150—151°, was identical with an authentic sample of 2-benzylquinoline picrate.[11] The benzene effluent was recrystallized from acetone to give 0.188 g (10.4%) of phenyl-di-(2-quinolyl)carbinol (**15**), colorless prisms, mp 176—177°. *Anal.* Calcd. for $C_{25}H_{18}ON_2$: C, 82.84; H, 5.01; N, 7.73. Found: C, 83.04; H, 4.81; N, 7.90. IR ν_{max}^{Nujol} cm^{-1}: 3400 (OH). NMR τ ($CDCl_3$): 1.95—2.8 (m). Mass Spectrum *m/e*: 362 (M^+). Further elution with ether and that with MeOH gave 0.044 g (3.4%) of **4** and 0.01 g (0.7%) of **3**, respectively.

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