

Reaction of 2,6-Dibutylaminohepta-2,5-dien-4-one with Malononitrile

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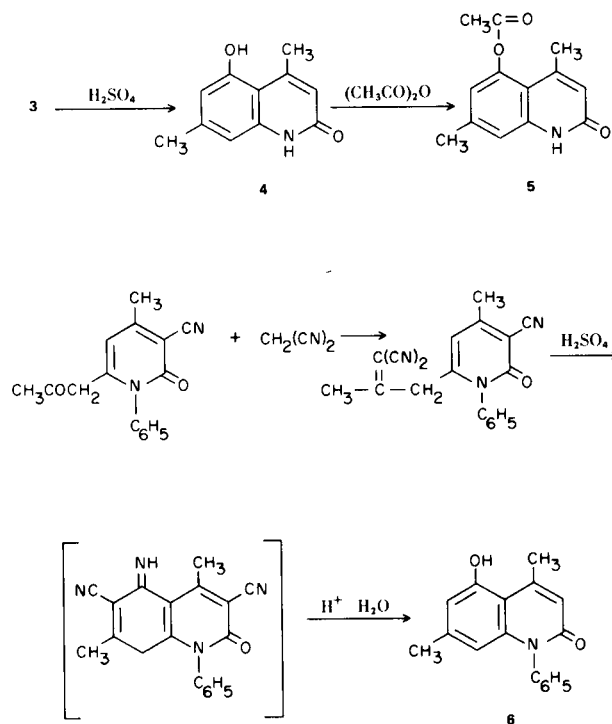
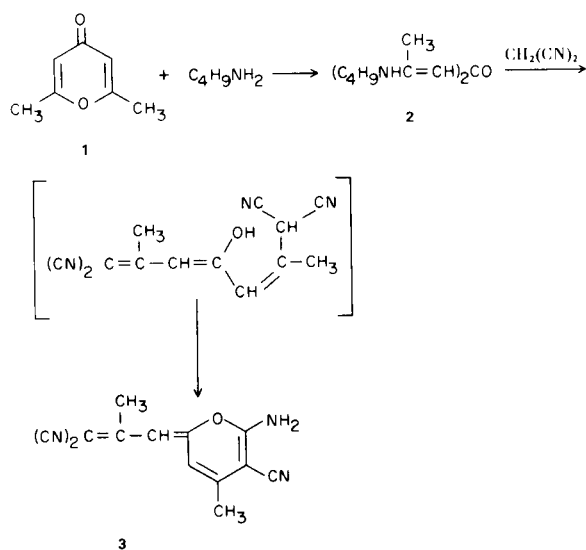
Malononitrile reacted with the title compound to give 6-amino-5-cyano-2-(3,3-dicyano-2-methylallylidene-4-methyl-2H-pyran) (3). Treatment of 3 with hot 80% sulfuric acid yielded 4,7-dimethyl-5-hydroxy-2(1H)quinolone. With concentrated aqueous sodium hydroxide, 3 gave 5-amino-3,6-dicyano-4,7-dimethyl-2(1H)quinolone and 5-amino-6-carbamoyl-3-cyano-4,7-dimethyl-2(1H)quinolone. The reaction of 3 with hydrochloric in acetic acid gave a mixture of 6-amino-3,7-dicyano-2,8-dimethyl-4-quinolizone and 3-cyano-4-methyl-6-(3,3-dicyano-2-methylallyl)-2-pyrone. Compound 3 also reacted with methylamine, butylamine and piperidine to give 8-amino-5-cyano-4-methyl-2-pyridone, 6-butylamino-5-cyano-4-methyl-2-pyridone and 5-cyano-4-methyl-6-piperidino-2-pyridone respectively.

We have shown (1) that 2,6-dimethyl-4-pyrone (1) reacted with malononitrile to give 4-dicyanomethylene-2,6-dimethyl-4H-pyran which in turn reacted with primary amines to give 1,4-dihydropyridine and copyrine derivatives. The present paper describes the results that were obtained when these two reactions were reversed; *i.e.*, 1 was allowed to react first with a primary amine and then the reaction product was allowed to react with malononitrile.

We have reported (2) that 1 reacted with *n*-butylamine to give the dienamine 2, and now it has been found that malononitrile reacts rapidly with 2 in alcohol at room temperature to give a red product which has been assigned the structure 3. The formation of 3 presumably occurred

by displacement of both of the butylamino groups of 2 by malononitrile to give the bracketed intermediate, which in turn cyclized to give 3.

Compound 3 was assigned the structure indicated for the following reasons: (a) its electronic absorption spectrum showed absorption at 512 nm, suggesting a long conjugated chain separating donor and acceptor groups; (b) the ir spectrum showed strong absorption at 3 μ for

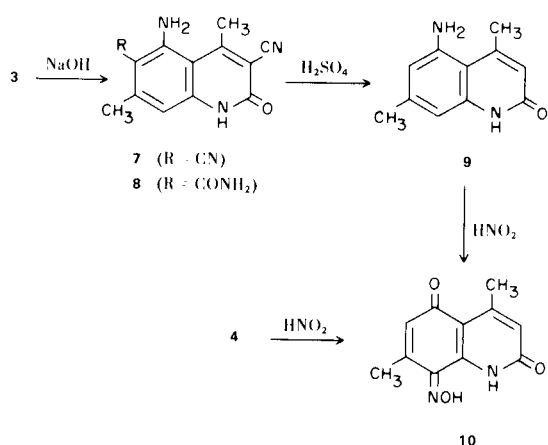


the amino group; (c) the nmr and mass spectra (see experimental section) were in agreement with structure **3**; (d) the chemical transformations to be discussed in the following sections were consistent with structure **3**.

Compound **3** underwent some interesting rearrangements when treated with acids or bases. These reactions and the structures of the rearrangement products will be described first, and then possible reaction paths leading to these products will be considered.

The reaction of **3** with hot 80% sulfuric acid yielded 4,7-dimethyl-5-hydroxy-2(1*H*)quinolone (**4**), which on acetylation gave the 5-acetoxy compound **5**. We were unable to prepare **4** by an alternative route, but the closely related 1-phenyl derivative, **6**, was prepared (3). The electronic spectra of **4** and **6** show a single maximum at 290 nm and 298 nm, respectively, indicating similar structures.

Treatment of **3** with concentrated aqueous sodium hydroxide gave the 2(1*H*)quinolone derivatives **7** and **8**. Hydrolysis of **7** and **8** with sulfuric acid resulted in the formation of **9**. An attempt to convert the amine **9** to the hydroxy derivative **4** by treatment of **9** with nitrous acid resulted not only in the desired conversion, but also in nitrosation, since **10** was the product. Treatment of **4** with nitrous acid also gave **10**. The nitrosation product **10** was assigned the oxime rather than the nitroso structure because the mass spectrum showed a large peak for the loss of OH, which suggests an oxime.

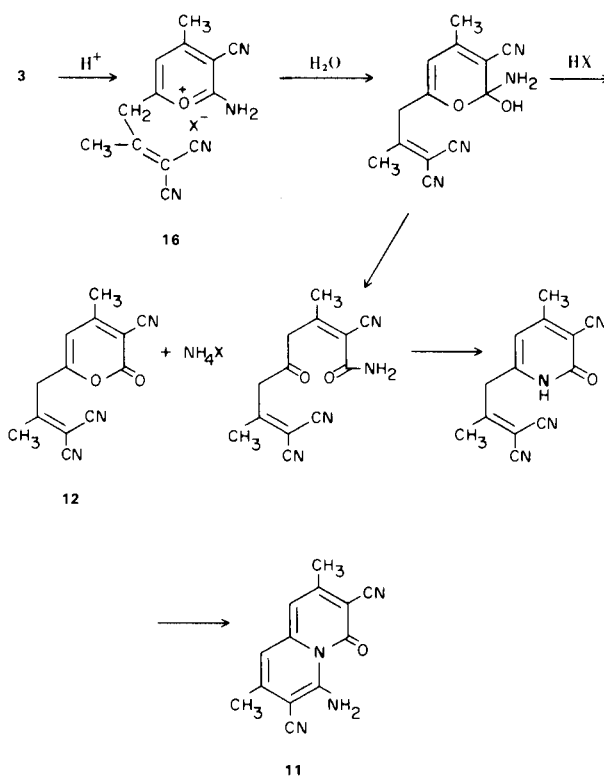


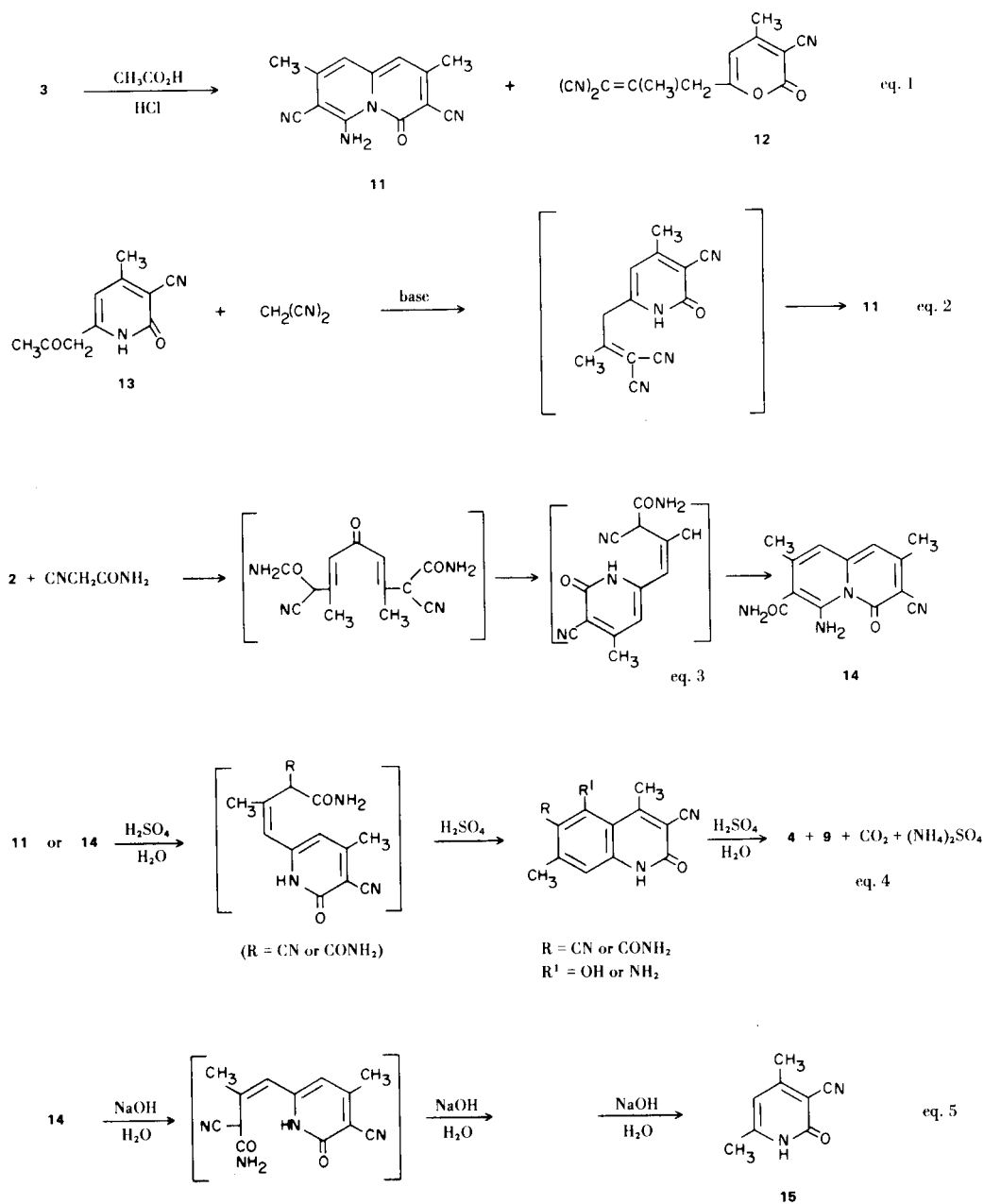
The reaction of **3** with hydrochloric in acetic acid gave a mixture of the quinolizone derivative, **11**, and the 2-pyrone, **12** (eq. 1). Compound **11** was also prepared from 6-acetyl-3-cyano-4-methyl-2-pyridone (**13**) and malononitrile (eq. 2). Compound **14**, which is closely related to **11**, was prepared from **2** and cyanoacetamide (eq. 3), and **11** and **14** were found to give similar electronic absorption spectra (see Experimental). Both **11** and **14** were converted to **4** along with a small amount

of **9** by treatment with hot 80% sulfuric acid, evidently through ring opening of the quinolizone followed by cyclization into the 5-position of the pyridone (eq. 4). Another example of ring opening of the quinolizone was the formation of 3-cyano-4,6-dimethyl-2-pyridone (**15**) by the hydrolysis of **14** with aqueous sodium hydroxide (eq. 5), which presumably takes place through hydrolysis of the amidine bond followed by a reverse Knoevenagel reaction and hydrolysis of an activated ketone. The quinolizones **11** and **14** show electronic absorption spectra that are similar to those of other 4-quinolizones (4). A quinolizone such as **11** can be distinguished from the isomeric 2(1*H*)quinolone **7** by the nmr spectra, since **11** shows two protons in the aromatic region and **7** shows one proton.

Before discussing any more reactions of **3**, we will attempt to present logical reaction paths for the products that were obtained from **3** with sulfuric acid, sodium hydroxide, and the acetic acid/hydrochloric acid combination. Although we have no proof that the quinolizone (**11**) was formed as an intermediate from the reaction of **3** with sulfuric acid, we will consider it to be the primary product that was formed from **3** with acidic reagents. A reasonable mechanism for the formation of **11** (as well as **12**) follows, including the known fact (from nmr spectrum) that **3** is protonated to give the allylpyrylium salt **16**.

If our assumption is correct that **11** was an intermediate

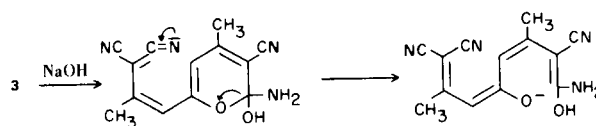


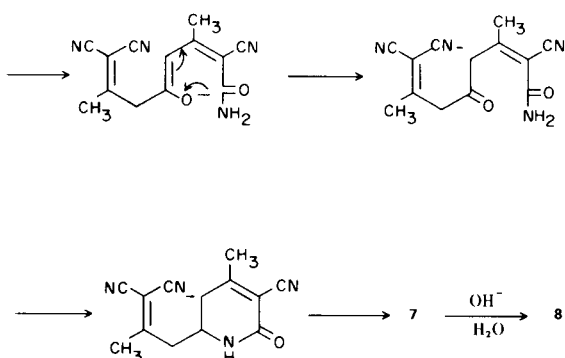


during the reaction of **3** with sulfuric acid, then the formation of the final product **4** could be explained by the route which was previously described in eq. 4. The formation of the small amount of **9** that was isolated from the reaction of **11** with sulfuric acid could have been overlooked in the earlier reaction that was carried out with **3** and sulfuric acid owing to the different methods used to work up the reactions.

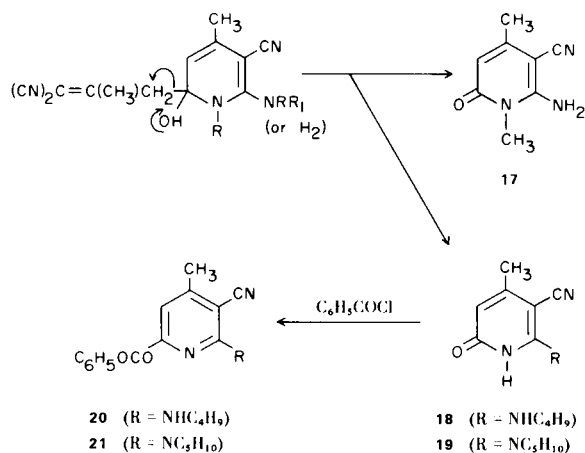
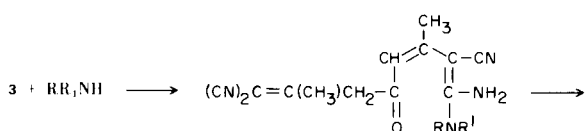
It was found that **3** dissolves in aqueous sodium hydroxide to give a colored solution from which **3** was regenerated on acidification. However, heating the basic solution

caused the color to fade, and the products **7** and **8** were obtained when the solution was acidified. One possible reaction scheme for the conversion of **3** to **7** and **8** is the following:





Compound **3** also reacted with methylamine, butylamine and piperidine to give the pyridones **17**, **18**, and **19**, respectively. We assume that **3** reacted with the amines in the following way:



We have assigned the structures **17**, **18**, and **19** on the basis of their ir spectra and on benzylation experiments, but we can give no explanation for the difference in behavior between methyl- and butylamine. The ir spectrum of **17** showed an NH₂ doublet and **17** did not undergo benzylation. Compound **18** showed an NH band and gave the oxygen benzyolated product **20** (NH and ester absorption). Oxygen acylation also occurred with **19** giving **20** (ester absorption). Similar oxygen acylation has been shown to take place with 2-pyridones (5). The electronic absorption spectra of the pyridones **17**, **18** and **19** are similar, indicating that they have the same generic structure.

EXPERIMENTAL (6)

6-Amino-5-cyano-2-(3,3-dicyano-2-methylallylidene)methyl-2H-pyran (**3**).

A solution of 0.1 mole of 2,6-dibutylaminohepta-2,5-dien-4-one (**2**) in 80 ml. of alcohol was added to a solution of 0.2 mole of malononitrile in 80 ml. of alcohol. The mixture immediately turned red and a solid separated. The solid was collected and crystallized from pyridine giving 15 g. of **3**, m.p. 252-253°.

The λ max ($\epsilon \times 10^{-3}$) in acetonitrile are 230 (8.7), 300 (5.0), 340 (6.0), 485 (30.5), and 512 nm (30.0).

The mass spectral data for **3** are: 238 (100) [M⁺]; 237 (17) [M-H]; 223 (5) [M-CH₃]; 210 (4) [M-CO]; 209 (5) [M-HCO]; 196 (10) [m/e 223-HCN]; 195 (10) [m/e 223-CO]; 194 (8) [m/e 223-HCO]; and 173 (11) [M-CH(CN)₂].

The nmr spectrum in dimethylsulfoxide d₆ (DMSO-d₆) shows the methyl group in the side chain at δ 2.05 (broadened S, 3H), the methyl group in the 4-position at δ 2.32 (S, 3H), the proton in the 5-position at δ 5.53 (S, 1H), the proton in the side chain at δ 6.1 (broadened S, 1H), and NH₂ at δ 9.2 ppm (broad S, 2H). The nmr spectrum was also run in deuterated trifluoroacetic acid, and protonation was found to take place on the methyldyne carbon adjacent to the ring: CH₃ in side chain δ 2.52 (S, 3H), CH₃ at 4-position δ 2.82 (S, 3H), CH₂ adjacent to ring δ 4.27 (S, 2H), and proton in 5-position δ 7.25 ppm (S, 1H).

Anal. Calcd. for C₁₃H₁₀N₄O: C, 65.5; H, 4.2; N, 23.5. Found: C, 65.5; H, 4.4; N, 23.2.

5-Hydroxy-4,7-dimethyl-2(1H)quinolone (**4**).

Method A.

A mixture of 0.01 mole of (**3**) and 25 ml. of 80% sulfuric acid was refluxed until bubbling stopped (about one-half hour). The solution was poured into water, and the solid was collected and dissolved in dilute sodium hydroxide. After removal of any insoluble material by filtration, the solution was acidified with acetic acid, and the solid was collected and crystallized from acetic acid yielding 1 g. of **4**, m.p. 307-309°.

Method B.

A mixture of 0.01 mole of 6-amino-3,7-dicyano-2,8-dimethyl-4-quinolizone (**11**) and 20 ml. of 80% sulfuric acid was allowed to react by the procedure described in Method A giving 0.8 g. of **4**, m.p. 308-310°.

Method C.

The procedure described for Method B was repeated using 6-amino-7-carbamoyl-3-cyano-2,8-dimethyl-4-quinolizone (**14**) with essentially the same results.

The λ max ($\epsilon \times 10^{-3}$) for **4** in dimethylformamide (DMF) was 290 nm (12.2).

The mass spectral data for **4** are: 189 (100) [M⁺]; 161 (28) [M-CO]; 160 (43) [M-HCO]; 133 (3) [m/e 161-CO]; and 132 (4) [m/e 161-HCO].

The nmr spectrum in DMSO-d₆ shows the 4-CH₃ at δ 2.30 (S, 3H), the 7-CH₃ at δ 2.74 (S, 3H), H in 3-position at δ 6.20 (S, 1H), 6-H at δ 6.48 (S, 1H), 8-H at δ 6.68 (S, 1H), and the OH (or NH) at δ 11.4 ppm (broad S, 1H).

Anal. Calcd. for C₁₁H₁₁NO₂: C, 69.8; H, 5.9; N, 7.4. Found: C, 69.8; H, 5.7; N, 7.2.

5-Acetoxy-4,7-dimethyl-2(1H)quinolone (**5**).

A mixture of 0.01 mole of **4** and 20 ml. of acetic anhydride was boiled until the solid dissolved (about 5 minutes), the solution

was cooled, and the solid was collected and crystallized from acetic anhydride giving 1.5 g. of **5**, m.p. 264-265°.

The mass spectral data for **5** are: 231 (32) [M^+]; 189 (100) [M-CH₂CO]; 161 (17) [189-CO]; 160 (23) [189-HCO]; 133 (2) [161-CO]; 132 (3) [160-CO]; 43 (21) [CH₃CO].

Anal. Calcd. for C₁₃H₁₃NO₃: C, 67.5; H, 5.7; N, 6.1. Found: C, 67.5; H, 5.7; N, 6.4.

4,7-Dimethyl-5-hydroxy-1-phenyl-2(1H)quinolone (6).

A mixture of 2.6 g. of 3-cyano-4-methyl-1-phenyl-6-acetylpyrone (7), 1 g. of malononitrile, 0.8 g. of ammonium acetate, 2 ml. of acetic acid and 50 ml. of chloroform was refluxed using a water separator for 1 hour. The reaction mixture was filtered hot, and the solid was crystallized from acetonitrile containing a small amount of acetic acid to yield 2.2 g. of 3-cyano-6-(3,3-dicyano-2-methylallyl-4-methyl-1-phenyl-2-pyrone, m.p. 302-303°. The λ max ($\epsilon \times 10^{-3}$) in methylene chloride was 337 nm (15.8).

Anal. Calcd. for C₁₉H₁₄N₄O: C, 72.6; H, 4.5; N, 17.8. Found: C, 72.4; H, 4.2; N, 17.7.

A mixture of 1 g. of the above pyrone and 40 ml. of 80% sulfuric acid was refluxed for 10 minutes and the solid was collected and crystallized from aqueous alcohol giving 0.7 g. of **6**, m.p. 299-300°.

The λ max ($\epsilon \times 10^{-3}$) in DMF was 298 nm (11.5).

The mass spectral data for **6** are: 265 (92) [M^+]; 264 (100) [M-1]; 250 (37) [M-CH₃]; 237 (12.5) [M-CO]; 236 (25) [M-HCO]; 160 (12.5).

The nmr spectrum in DMSO-d₆ shows the 4-CH₃ at δ 2.12 (S, 3H), the 7-CH₃ at δ 2.71 (S, 3H), 3-H at δ 5.85 (S, 1H), 6-H at δ 6.35 (S, 1H), 8-H at δ 6.61 (S, 1H), and phenyl protons δ 7.23-7.74 ppm (M, 5H).

Anal. Calcd. for C₁₇H₁₅NO₂: C, 77.0; H, 6.0; N, 5.3. Found: C, 76.8; H, 5.7; N, 5.4.

5-Amino-3,6-dicyano-4,7-dimethyl-2(1H)quinolone (7).

A mixture of 5 g. of **3** and 35 ml. of 25% aqueous sodium hydroxide was heated to boiling and 75 ml. of water was added in portions with heating over a period of 5 minutes. The clear solution was cooled and 35 ml. of acetic acid was added. The solid that separated was washed with water and crystallized from acetic acid giving 1.5 g. of **7**, m.p. 370-371°.

The λ max ($\epsilon \times 10^{-3}$) in DMF are \sim 320 (27.5), 330 (32.8), and 380 nm (14.0).

The mass spectral data for **7** are: 238 (100) [M^+]; 237 (2) [M-H]; 210 (3) [M-CO]; 205 (5) [M-HCO]; 182 (1) [210-CO]; 181 (1) [209-HCO].

The nmr spectrum in DMSO-d₆ shows the 4-CH₃ at δ 2.47 (S, 3H), 7-CH₃ at δ 2.90, and the 8-H at δ 6.45 ppm (S, 1H).

Anal. Calcd. for C₁₃H₁₀N₄O: C, 65.5; H, 4.2; N, 23.5. Found: C, 65.3; H, 4.6; N, 23.2.

5-Amino-6-carbamoyl-3-cyano-4,7-dimethyl-2(1H)quinolone (8).

The mother liquors from the preparation of **7** were diluted with 50 ml. of water and allowed to stand overnight. The solid that separated was collected and crystallized from isopropyl alcohol giving 1 g. of **8**, m.p. 338-339°.

The λ max ($\epsilon \times 10^{-3}$) in DMF are 305 (17.5), 315 (18.0), and 350 nm (12.1).

The mass spectral data for **8** are: 256 (50) [M^+]; 239 (100) [M-NH₃]; 212 (14) [M-CONH₂]; 211 (18) [239-CO]; 210 (23) [239-HCO]; 184 (23); 183 (27); and 156 (18).

The nmr spectrum in DMSO-d₆ shows the 4-CH₃ at δ 2.47 (S, 1H); the 7-CH₃ at δ 2.72 (S, 1H), the 8-H at δ 6.59, and three exchangeable protons at δ 5.55, 7.70, and 8.00 ppm.

Anal. Calcd. for C₁₃H₁₂N₄O₂: C, 60.9; H, 4.7; N, 21.9. Found: C, 60.8; H, 4.8; N, 21.6.

5-Amino-4,7-dimethyl-2(1H)quinolone (9).

Method A.

A mixture of 2 g. of **7** or **8** and 30 ml. of 80% sulfuric acid was refluxed for 15 minutes, cooled and poured onto ice, giving the sulfate salt of **9**. The salt was dissolved in hot water, the solution was made basic with ammonium hydroxide, and the solid that separated was collected and crystallized from water yielding 0.6 g. of **9**, m.p. 224-226°.

Method B.

A mixture of 1 g. of **11** or **14** and 10 ml. of 80% sulfuric acid was refluxed for 1 hour, cooled and poured onto ice. The solid was collected and extracted with boiling water. The extract was cooled, the solid that separated was collected and dissolved in hot water, and the solution made basic with ammonium hydroxide. The solid was collected (0.1 g., m.p. 223-225°) and shown to be identical (by ir) with **9** obtained by Method A. Extraction of the water-insoluble material with boiling alcohol gave 0.2 g. of **4**.

The λ max ($\epsilon \times 10^{-3}$) in DMF are \sim 290 (24.9) and \sim 330 nm (12.4).

The mass spectral data for **9** are: 188 (100) [M^+]; 187 (14) [M-1]; 173 (3) [M-CH₃]; 171 (4) [M-NH₃]; 170 (8); 169 (6); 161 (16) [M-HCN]; 160 (22) [M-CO]; and 159 (22) [M-HCO].

The nmr spectrum in DMSO-d₆ shows the 4-CH₃ at δ 2.3 (S, 1H), the 7-CH₃ at δ 2.71 (S, 1H), and the three aromatic protons as singlets at δ 6.25, 6.47 and 6.87 ppm.

Anal. Calcd. for C₁₁H₁₂N₂O: C, 70.2; H, 6.4; N, 14.9. Found: C, 70.0; H, 6.6; N, 14.7.

8-Hydroxyimino-4,7-dimethyl-2,5(1H,8H)quinolinedione (10).

Method A.

A solution of 2 g. of **4** in 50 ml. of acetic acid plus 3 ml. of sulfuric acid was stirred, and 1 g. of sodium nitrite dissolved in 5 ml. of water was slowly added. The solid was collected and crystallized from acetic acid yielding 0.9 g. of **10**, m.p. 229-230°.

Method B.

A solution of 1 g. of **9** in 1 ml. of sulfuric acid and 50 ml. of water was prepared, and 0.5 g. of sodium nitrite in 5 ml. of water was slowly added to this solution. The solid was collected and crystallized giving 0.4 g. of **10**, m.p. 230-231°.

The λ max ($\epsilon \times 10^{-3}$) in DMF are 305 (25.0), \sim 350 (10.0) and 450 nm (3.5).

The mass spectral data are: 218 (100) [M^+]; 201 (67) [M-OH]; 190 (9) [M-CO]; 189 (10) [M-HCO]; 173 (16) [201-HCO]; and 172 (13) [201-H₂CO].

Anal. Calcd. for C₁₁H₁₀N₂O₃: C, 60.5; H, 4.6; N, 12.8. Found: C, 60.2; H, 4.5; N, 12.5.

6-Amino-3,7-dicyano-2,8-dimethyl-4-quinolizone (11).

Method A.

A mixture of 3 g. of **3**, 150 ml. of acetic acid, 3 ml. of concentrated hydrochloric acid and 3 ml. of water was refluxed for 5 minutes, diluted with 50 ml. of water, and the solid was collected and crystallized from pyridine giving 0.9 g. of **11**, m.p. 335-336°.

Method B.

A mixture of 2 g. of 6-acetyl-3-cyano-4-methyl-2-pyridone (**13**) (7), 1.6 g. of malononitrile, 20 ml. of methyl alcohol and

10 ml. of 10% methanolic potassium hydroxide was refluxed for 1 hour, cooled, and the solid was crystallized from pyridine giving 1.2 g. of **11**, m.p. 335-336°.

The λ max ($\epsilon \times 10^{-3}$) in DMF are 300 (4.0), 360 (5.0) and 473 nm (34.0).

The mass spectral data are: 238 (100) [M^+]; 210 (72) [M-CO]; 209 (22) [M-HCO]; 195 (7); 119 (7) [M^{++}]; 105 (5) [(M-CO) $^{++}$]; 78 (8).

The nmr spectrum in DMSO- d_6 shows CH_3 at δ 2.32 (S, 6H), the proton in the 1- or 9-position at δ 6.27 (S, 1H), and the other of these two protons at δ 6.48 ppm (S, 1H).

Anal. Calcd. for $C_{13}H_{10}N_4O$: C, 65.5; H, 4.2; N, 23.5. Found: C, 65.6; H, 4.2; N, 23.4.

3-Cyano-4-methyl-6-(3,3-dicyano-2-methylallyl)-2-pyrone (**12**).

The mother liquors from Method A for the preparation of **11** were evaporated to dryness and the residue was washed with alcohol. Crystallization from alcohol afforded 1 g. of **12**, m.p. 149-150°.

The λ max ($\epsilon \times 10^{-3}$) in acetonitrile are 210 (16.0), 310 (8.7), and 518 nm (40.4).

The mass spectral data are: 239 (7) [M^+]; 211 (2) [M-CP]; 134 (97) [M-CH₂C(CH₃)=C(CN)₂]; 78 (100) [134-C₂O₂]; 51 (26) [78-HCN].

The nmr spectrum in deuteriochloroform shows a CH_3 at δ 2.42 (S, 3H), another CH_3 at δ 2.52 (S, 3H), the C=CCH₂ at δ 3.88 (S, 2H), and the proton in the 5-position at δ 6.43 ppm (S, 1H).

Anal. Calcd. for $C_{13}H_9N_3O_2$: C, 65.3; H, 3.8; N, 17.6. Found: C, 65.0; H, 3.9; N, 17.5.

6-Amino-7-carbamoyl-3-cyano-2,8-dimethyl-4-quinolizone (**14**).

A mixture of 2 g. of **2**, 1.5 g. of cyanoacetamide and 20 ml. of alcohol was refluxed for 2 hours, and the solid was collected and crystallized from acetic acid giving 1.2 g. of **14**, m.p. 312-313°.

The λ max ($\epsilon \times 10^{-3}$) in DMF are 298 (6.4), 355 (4.5), and 468 nm (25.0).

The mass spectral data are: 256 (92) [M^+]; 239 (83) [M-OH]; 238 (17); 211 (100) [239-CO]; 210 (23); and 185 (17).

Anal. Calcd. for $C_{13}H_{12}N_4O_2$: C, 60.9; H, 4.7; N, 21.9. Found: C, 60.5; H, 4.8; N, 21.6.

3-Cyano-4,6-dimethyl-2-pyridone (**15**).

A mixture of 2 g. of **14** and 50 ml. of 2 N sodium hydroxide was refluxed until the solid dissolved. The solution was cooled, neutralized with acetic acid, and the solid was collected and crystallized from acetic acid giving 0.7 g. of **15**, m.p. 285-287°. The reported (8) m.p. is 286°.

6-Amino-5-cyano-4-methyl-2-pyridone (**17**).

A mixture of 2 g. of **3**, 10 ml. of alcohol and 2 ml. of 40% aqueous methylamine was heated until the solid dissolved. The solution was cooled and the resulting solid was crystallized from alcohol yielding 1.1 g. of **17**, m.p. 291-292°.

The λ max ($\epsilon \times 10^{-3}$) in acetonitrile are 270 (14.5) and 314 nm (10.5).

The mass spectral data are: 163 (100) [M^+]; 135 (30) [M-CO]; 134 (23) [M-HCO]; 122 (6); 120 (17); and 93 (6).

The nmr spectrum in DMSO- d_6 shows the 4-CH₃ at δ 2.12 (S, 3H), the 1-CH₃ at δ 3.3 (S, 3H), the proton in the 3-position at δ 5.53 (S, 1H) and the NH₂ at δ 7.2 ppm (broad S, 2H).

Anal. Calcd. for $C_8H_9N_3O$: C, 58.9; H, 5.6; N, 25.8. Found: C, 59.1; H, 5.6; N, 25.8.

6-Butylamino-5-cyano-4-methyl-2-pyridone (**18**).

A mixture of 2 g. of **3**, 10 ml. of pyridine and 3 ml. of butylamine was heated on a steam bath for 1 hour, poured into water, and the solid was collected and crystallized from ethoxy-ethanol giving 1.6 g. of **18**, m.p. 249-250°.

The λ max ($\epsilon \times 10^{-3}$) in acetonitrile are 265 (14.0) and 320 nm (12.5).

The mass spectral data are: 205 (M^+) [23]; 176 (M-C₂H₅ or HCO) [11]; 162 (100) [M-C₃H₇]; 149 (19) [M-C₄H₈]; and 30 (CH₃NH) [31].

Anal. Calcd. for $C_{11}H_{15}N_3O$: C, 64.4; H, 7.4; N, 20.5. Found: C, 64.4; H, 7.1; N, 20.7.

5-Cyano-4-methyl-6-piperidino-2-pyridone (**19**).

This compound was prepared by the procedure described for the preparation of **18** using piperidine rather than butylamine. The product (1.5 g.) was crystallized from alcohol, m.p. 219-220°.

The λ max ($\epsilon \times 10^{-3}$) in acetonitrile are 270 (10.8) and 324 nm (7.1).

The mass spectral data are: 217 (100) [M^+]; 216 (37) [M-H]; 202 (4) [M-CH₃]; 188 (56) [M-HCO]; 176 (9) [M-C₃H₅]; 175 (7) [M-C₃H₆]; 174 (16) [M-C₃H₇]; 162 (16) [M-C₄H₇]; and 161 (12) [M-C₄H₉].

The nmr spectrum in DMSO- d_6 shows the piperidino protons as two singlets at δ 1.55 and 3.41, the 4-CH at δ 2.13 (S, 3H), and the 3-H at δ 5.75 ppm (S, 1H).

Anal. Calcd. for $C_{12}H_{15}N_3O$: C, 66.3; H, 7.0; N, 19.3. Found: C, 66.3; H, 7.1; N, 19.4.

2-Benzoyloxy-6-butylamino-5-cyano-4-methylpyridine (**20**).

A mixture of 2 g. of **18**, 1.5 ml. of benzoyl chloride and 10 ml. of pyridine was heated on a steam bath for 30 minutes and poured into water. Crystallization of the solid yielded 1.8 g. of **20**, m.p. 134-135°.

The mass spectral data are: 309 (4) [M^+]; 267 (3) [M-C₃H₆]; 266 (2) [M-C₃H₇]; 253 (1) [M-C₄H₈]; 204 (3) [M-C₆H₅CO]; and 188 (5) [M-C₆H₅CO₂]; 105 (100) [C₆H₅CO]; and 77 (30) [C₆H₅].

The nmr spectrum in deuteriochloroform shows the butyl group as three multiplets at δ 1.0, 1.65 and 3.5, the 4-CH₃ at δ 2.48 (S, 3H), the 3-H at δ 6.45 (3, 1H) and the aromatic protons at 7.55-8.43 ppm (M, 5H).

Anal. Calcd. for $C_{18}H_{19}N_3O_2$: C, 70.0; H, 6.2; N, 13.6. Found: C, 70.4; H, 6.4; N, 13.4.

2-Benzoyloxy-5-cyano-4-methyl-6-piperidinopyridine (**21**).

Compound **21** was prepared from **19** and benzoyl chloride by the procedure described for the preparation of **20** and melted at 119-120° (from alcohol).

The mass spectral data are: 321 (53) [M^+]; 216 (100) [M-C₆H₅CO]; 188 (18) [216-CO or C₂H₄]; 105 (36) [C₆H₅CO]; 84 (10) [C₅H₁₀N]; and 77 (37) [C₆H₅].

Anal. Calcd. for $C_{19}H_{19}N_3O_2$: C, 71.0; H, 6.0; N, 13.1. Found: C, 70.6; H, 6.2; N, 13.5.

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REFERENCES

- (1) J. A. Van Allan, G. A. Reynolds, C. C. Petropoulos, and D. P. Maier, *J. Heterocyclic Chem.*, **7**, 495 (1970).
- (2) J. A. Van Allan, G. A. Reynolds, J. Alessi, S. C. Chang, and R. C. Joines, *J. Heterocyclic Chem.*, **8**, 919 (1971).
- (3) An interesting observation that has been found to be typical of *N*-phenyl-2-pyridones is that the mass spectra show a parent minus one *m/e* which is larger than the parent peak and is probably due to an ion radical formed by the cyclization of the oxygen atom into the *ortho* position of the phenyl ring.
- (4) F. Bohlmann, N. Ottawa and R. Keller, *Ann. Chem.*, **587**, 167 (1954).
- (5) R. Adams, J. Hine and J. Campbell, *J. Am. Chem. Soc.*, **71**, 387 (1949).
- (6) The nmr spectra were measured at 60 MHz on a Varian A-60 spectrometer with tetramethylsilane as an internal standard. The electronic spectra were determined with Cary Model 14 and 15 spectrophotometers. The mass spectra were determined using a Consolidated Electrodynamics Model 21-110B instrument, and the data are reported as mass (relative intensity) [assignment].
- (7) Reactions of 4-Methoxypyrylium Salts with Secondary Amines, J. A. Van Allan, G. A. Reynolds and C. C. Petropoulos, to be submitted for publication in *J. Heterocyclic Chem.*
- (8) W. Reed and A. Meyer, *Chem. Ber.*, **90**, 2841 (1957).