The Synthesis of 2-Pyridones from Cyclic Cyano Ketones. A New Aromatization Procedure for Dihydro-2-pyridones[1]

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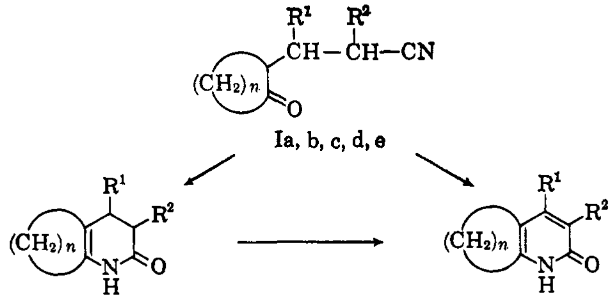
Treatment of 2-(2-cyanoalkyl)cyclohexanones with 96% sulfuric acid for several hours at room temperature results in the formation of the corresponding cycloalkano[*e*]-2-pyridones by means of a consecutive cyclization–aromatization. Similar treatment of 3,4-dihydro-2-pyridones obtained by another route also leads to the 2-pyridones. The cyclization reaction is considered to be a further extension of the Ritter reaction, whereas the aromatization process appears to be novel.

During the course of a study directed toward the use of certain polyfunctional nitriles[3] in azasteroid synthesis, it was necessary to determine the behavior of various cyanoalkyl cyclohexanones and cyclopentanones (I) in sulfuric acid. It was found that cold 5–30% solutions of simple nitriles (cyanoethylcyclopentane and cyanoethylcyclohexane) and chloronitriles (4-chlorobutyronitrile and 2-chlorocyanoethylcyclohexane and -cyclopentane) in sulfuric acid could be recovered unchanged by dilution with water after 1–2 hr. with very little loss of material (10%). However, when 2-(2-cyanoethyl)cyclohexanone (Ib) was added to cold sulfuric acid and allowed to stand at 0–3° for 2 hr., there was no keto nitrile in the diluted solution. Instead, two crystalline products were recovered, one from the acid solution, the other from the neutralized solution. The product obtained from the extraction of the dilute acid solution showed infrared absorption at 3.15, 3.25 and 6.05 μ, all typical of the amide grouping but no bands attributable to a keto group. The ultraviolet spectrum exhibited only a single maximum at 254 mμ (ε 5020). This data excluded the possibility of the product being the corresponding keto amide IV which would have arisen from partial hydrolysis of the nitrile group. The n.m.r. spectrum[4] in deuteriochloroform exhibited a *single* proton signal at 575 c.p.s., which vanished when the sample was treated with deuterated water. The lack of further deuterium exchange led to the assigned structure, IIb, 3,4,5,6,7,8-hexahydro-2-quinoline. A search of the literature revealed that this product was prepared[5] from the same keto nitrile using methanolic potassium hydroxide in *t*-butyl alcohol. Comparison of the products obtained from both routes confirmed their identity.


Ia, b, c, d, e

IIa,b,c,d,e

IIIa,b,c,d,e

a, $R^1 = H, R^2 = H, n = 3$
b, $R^1 = H, R^2 = H, n = 4$
c, $R^1 = H, R^2 = H, n = 5$
d, $R^1 = CH_3, R^2 = H, n = 4$
e, $R^1 = H, R^2 = CH_3, n = 4$

The second product isolated from the sulfuric acid treatment of the keto nitrile Ib formed a picrate in the usual manner and exhibited spectral properties rather different from the previous compound, IIb. The infrared spectrum revealed two strong carbonyl bands at 6.05 and 6.20 μ, as well as N–H absorption at 3.1 and 3.2 μ. The ultraviolet spectrum, $\lambda_{\max}^{\mathrm{EtOH}}$ 318 mμ (ε 6500), strongly suggested an aromatic system and the n.m.r. spectrum confirmed this. The n.m.r. spectrum indicated methylene protons (multiplet, centered at 112 c.p.s.), allylic protons (multiplet, centered at 165 c.p.s.), and vinyl protons (3-position, doublet at 392 c.p.s., $J_{\mathrm{H_3H_4}}$ = 9.8 c.p.s.; 4-position, doublet at 441 c.p.s., $J_{\mathrm{H_4H_3}}$ = 9.8 c.p.s.). The integrated ratio was 4:4:1:1. The N–H proton, which occurs at 805 c.p.s., was confirmed by exchange with heavy water. These data were all consistent with the structure of 5,6,7,8-tetrahydro-2-quinolone (IIIb). When a comparison of this product with that previously reported by Thesing and Muller[6] was made, both products proved to be identical.

The use of keto nitriles Id and Ie under these conditions led directly to the 4-methyl (IIId) and the 3-methyl (IIIe) derivatives of the tetrahydroquinolone. The structure of these products also was supported by their infrared and ultraviolet spectra which possessed the expected features and strongly resembled the parent compound, IIIb. The n.m.r. spectrum of IIIb, IIId, and IIIe are virtually identical except for the vinyl proton region. When the 4-position is substituted by methyl (IIId), the 441-c.p.s. doublet in IIIb disappears and the remaining 3-vinyl proton appears as a singlet at 377 c.p.s. Thus the low-field proton doublet in IIIb is due to the 4-H substituent. When the 3-position is substituted by methyl (IIIe), the 392-c.p.s. doublet vanishes and the signal at 424 c.p.s. is due to the lone proton at the 4-position. These values are all in close agreement with a variety of 1-methylpyridones studied by Elvidge and Jackman with regard to their aromaticity.[7] The NH proton for IIId and IIIe appears as a

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[1] This investigation is supported by a grant [RG-6248(C5)] from the National Institutes of Health.

[2] Research Associate, on leave from the Institute of Chemistry, Alonso Barba, Madrid, Spain.

[3] A. I. Meyers, J. Schneller, and N. K. Ralhan, *J. Org. Chem.*, **28**, 2944 (1963); A. I. Meyers and N. K. Ralhan, *ibid.*, **28**, 2950 (1963).

[4] All spectra were taken on the Varian A-60 instrument using tetramethylsilane as the internal standard.

[5] A. D. Campbell and I. D. R. Stevens, *J. Chem. Soc.*, 959 (1956).

[6] J. Thesing and A. Muller, *Ber.*, **90**, 711 (1957). We thank Dr. Thesing for supplying us with a sample of his quinolone.

[7] J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 860 (1961). Comparison of the products reported here with those of the present study allows a rough estimate of the aromaticity to be made by the same method. The values of τ_{obs} in the present study for positions 3, 4, 5, and 6 are very close ($\Delta\tau_{\mathrm{obs}}$ = 0.5 p.p.m.) to those reported by these authors. The models used for the calculation of degree of aromaticity as well as the method are given in ref. 7.

broad peak at 765 and 770 c.p.s., respectively, both disappearing rapidly upon the addition of deuterated water. A report[8] claims that the 4-methyl derivative (IIId) melts at 217–218°. The product obtained in the current report melts at 240–241°. In view of the data (infrared, ultraviolet, and n.m.r.) obtained here, there can be little doubt concerning the structure of these products.

That the hexahydro-2-quinolone (IIb) was indeed an intermediate in this reaction was demonstrated by treating it for 3 hr. in 96% sulfuric acid at room temperature and obtaining a 77% yield of the corresponding tetrahydro-2-quinolone (IIIb). There was present throughout the experiment a slow, constant evolution of sulfur dioxide indicating that the aromatization step involved reduction of sulfur from the +6 to the +4 state. An attempt to isolate the intermediates II when treating the keto nitriles with sulfuric acid always led to mixtures of the reduced (II) and oxidized (III) forms of the cyclic products. It was found advantageous to allow the keto nitriles to remain in the sulfuric acid for at least 3 hr. to ensure completion of the successive cyclization–aromatization process. The only exception found in this study was due to 2-(2-cyanoethyl)-cyclopentanone (Ia), which did not cyclize in the sulfuric acid, but was only hydrolyzed to the keto amide V. The latter product, however, was converted to the dihydro-2-pyridone (IIa) by neat heating at 170–180°, and this was readily aromatized to the 2-pyridone (IIIa) in sulfuric acid. In the case of 2-(2-cyanoethyl)cycloheptanone (Ic), it was necessary to allow the sulfuric acid-catalyzed condensation to proceed overnight to ensure complete reaction to the 2-pyridone (IIIc). Shorter reaction times always resulted in a mixture containing the dihydro-2-pyridone (IIc). In order to study the aromatization reaction in the absence of the cyclization process, the dihydro-2-pyridones (II) were prepared according to the method of Campbell and Stevens.[5] When the dihydro compounds (II) were treated with 96% sulfuric acid, they gave products (III) identical with those obtained directly from the series of keto nitriles I.

The initial formation of the hexahydro-2-quinolone (IIb) and dihydro-2-pyridones (II) may be represented as still a further extension of the Ritter reaction to the synthesis of N-heterocycles,[9,10] in which a nitrile can condense with an electrophilic site in sulfuric acid (Chart I). The Ritter reaction using the carbonyl group to generate the carbonium ion has already been described[11a] for simple nitriles and cyclic ketones to give analogous products (VI) as well as more complex materials.

With regard to the aromatization reaction, this process was examined further and found to proceed equally well in the absence of air (nitrogen) with the liberation of sulfur dioxide. When a quickly prepared solution (10^{-5} M) of the hexahydro-2-quinolone (IIb) in 96% sulfuric acid was inserted in a recording spectrophotometer, its spectrum changed rapidly (in less than 10 min.) from a single peak at 252 mμ to two peaks at 282 (sulfur dioxide) and 294 mμ (ϵ 8600) which was unchanged after 1 week. The rate of aromatization was slowed down considerably by the addition of either water or acetic acid to the sulfuric acid solution.[12] Because of the overlapping of the sulfur dioxide maximum upon the product maximum, as well as loss of sulfur dioxide from the cells, quantitative measurements were not feasible. Based upon the preceding observations, a mechanism for this process may be brought forward which involves initially a tautomeric shift of the hexahydro-2-quinolone (IIb) to the immonium form (VII) (Chart II). This is based on studies which have shown that amides protonate an oxygen rather than nitrogen in concentrated sulfuric acid.[11b] The transfer of two electrons from VII to sulfur trioxide or its solvate (disulfuric acid, $H_2S_2O_7$) is tentatively considered to be the rate-determining step. This is based upon the fact that the concentration of the acceptor is

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[8] A. Dornow and E. Neuse, *Arch. Pharm.*, **287**, 361 (1954).

[9] J. J. Ritter and P. P. Minieri, *J. Am. Chem. Soc.*, **70**, 4045, 4048 (1948).

[10] See ref. 3 and earlier references cited therein.

[11] (a) A. Y. Khorlin, O. S. Chizhov, and N. K. Kochektkov, *Zh. Obshch. Khim.*, **29**, 3411 (1959); (b) G. Fraenkel and C. Franconi, *J. Am. Chem. Soc.*, **82**, 4478 (1960).

[12] NOTE ADDED IN PROOF.—After the submission of this manuscript, two more references came to our attention regarding sulfuric acid-catalyzed cyclization of cyano ketones: O. Y. Magidson, *Zh. Obshch. Khim.*, **33**, 2173 (1963), and A. Vigier and J. Dreux, *Bull. soc. chim. France*, (**10**), 2293 (1963). Neither of these articles described the aromatization of the resulting dihydropyridones. The former paper reported the preparation of the 5,6-diphenyl derivative (X) which was also reported by us not to aromatize. The latter reference describes the transformation of a series of acyclic cyano ketones (A) to 3,4-dihydropyridones (B–F) using 90–92% sulfuric acid. Although it would be expected that B, E, and F should undergo aromatization to the α-pyridones under these conditions, our results indicate that the rate of aromatization in 90% sulfuric acid is about one-fortieth that in 97% acid. The reaction time reported by the French group for all the products was listed as 10 hr. We have observed that the oxidation is less than 20% complete after this period of time. Another fact that would account for the absence of the aromatized product in their report is the lack of ether solubility of the α-pyridones. These workers isolated their product by ether extraction, whereas we have found that only the dihydropyridones are ether soluble. This is presumably due to the zwitterionic character of the α-pyridones. See diagram below.

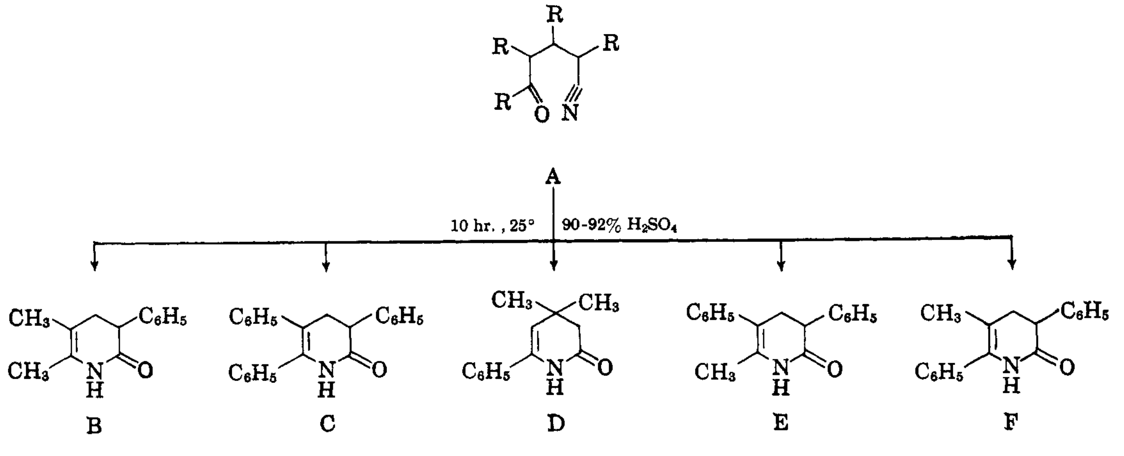


CHART I

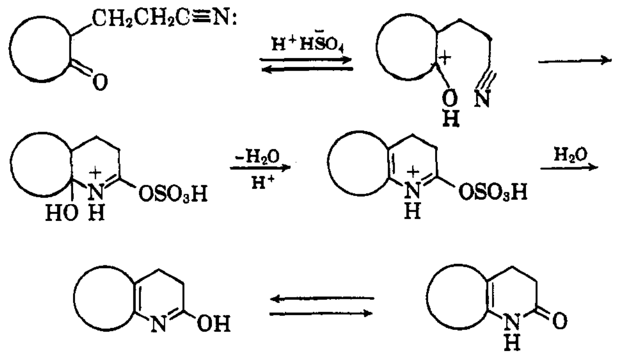
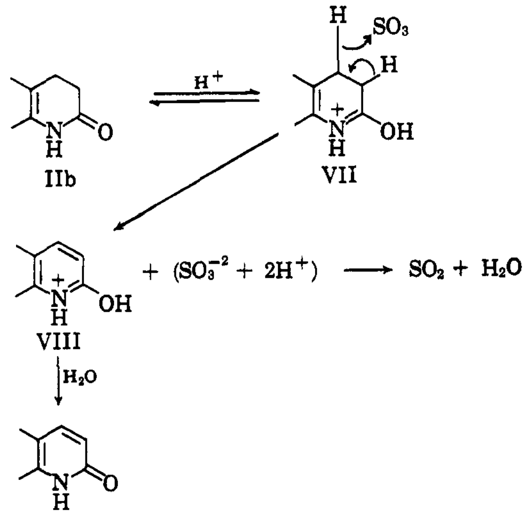
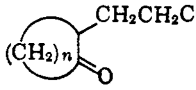


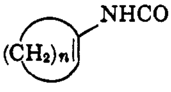
CHART II



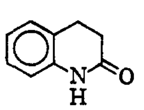
dependent upon the sulfuric acid concentration.[13] That is, the concentration of sulfur trioxide will be greatly reduced by the addition of a strong base such as water or acetic acid, thus lowering the rate of oxidation. A rapid removal of a proton by the solvent then gives rise to the aromatized product, VIII, which is isolated upon dilution with water.



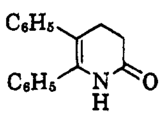
IV, $n = 4$
V, $n = 3$



VI, R = CH_3, C_6H_5
$n = 3, 4$



IX



X

When the dihydrocarbostyril (IX) and 5,6-disphenyl-3,4-dihydro-2-pyridone (X) were treated with sulfuric acid in the usual manner, no aromatization occurred. The major difference between the latter two compounds on all the others studied is the delocalization of the olefinic bond in the 5,6-position. Thus it appears that the decreased bond order in IX and X serve to deactivate the 4-position which is the one currently considered as being oxidized. It may appear questionable to describe the attack of the very electrophilic sulfur trioxide upon the σ bond at the 4-position when there is also available in the molecule a π bond at the 5,6-position. However, the driving force toward aromatization by VII could make the electrons at the 4-position very labile toward the highly electron-attracting sulfur atom.[14] All the keto nitriles employed in this study were prepared from the appropriate cyclo alkanone and α,β-unsaturated nitrile *via* the enamine intermediate.[15] Further studies to extend this reaction, both the cyclization and the aromatization, to more complex ring systems are currently in progress.

Experimental[16,17]

5,6,7,8-Tetrahydro-2-quinolone (IIIb). A. From **2-(2-Cyanoethyl)cyclohexanone** (Ib).—To 100 ml. of cold 96% sulfuric acid was added dropwise over a 2-hr. period 15.1 g. (0.1 mole) of the keto nitrile Ib. After the addition was complete, the reddish reaction mixture was allowed to warm to room temperature and stirring was maintained for an additional 3 hr. The mixture was poured over chipped ice; the resulting aqueous solution was extracted with chloroform[18] and then neutralized with ammonia. A white solid precipitated which was removed by extraction with chloroform. After drying with magnesium sulfate and removing the solvent, recrystallization of the residue from water yielded 8.1 g. (54%) of the product, m.p. 205–206°. A second recrystallization from ethyl acetate did not change the melting point. The infrared spectrum exhibited absorption at 3.1 and 3.3 (NH, NH assoc.) and 6.05 and 6.15 μ (C=O, C=N). The ultraviolet maximum appeared at 318 mμ (ethyl alcohol) (ϵ 6500).

Anal. Calcd. for $C_9H_{11}NO$: C, 72.48; H, 7.38; N, 9.39. Found: C, 72.55; H, 7.43; N, 9.52.

The **picrate** (from water) had m.p. 145–146°.

Anal. Calcd. for $C_{15}H_{14}N_4O_8$: C, 47.61; H, 3.70; N, 14.81. Found: C, 47.70; H, 3.93; N, 14.49.

B. From **3,4,5,6,7,8-Hexahydro-2-quinolone** (IIb).—To 4 ml. of cold sulfuric acid was added 0.6 g. (0.0039 mole) of the hexahydro-2-quinolone[6] (IIb); the mixture was stirred at room temperature for 3 hr. and made alkaline with ammonia after being poured over chipped ice and the solid removed as above. The product, obtained in 77% yield, was identical with that obtained from part A.

3-Methyl-5,6,7,8-tetrahydro-2-quinolone (IIIe). A. From **2-Methyl-3-(2-oxocyclohexyl)propionitrile** (Ie).—Ten grams (0.06 mole) of the cyano ketone was added slowly to 96% sulfuric acid at 0°. The solution, after completion of addition, was allowed to stir at room temperature for 3 hr. and then poured over chipped ice. Extraction of the aqueous acid solution with chloroform yielded 4.7 g. of the aromatized product, which after recrystallization from water melted at 210–211°. Neutralization of acidic solution with ammonia and extraction with chloroform yielded an additional 0.6 g. of the same material (m.p. 210–211°) isolated above. The total yield, 5.3 g. (54%) of IIId, possessed infrared absorption at 3.0 (NH) and 6.1 and 6.2 μ (C=O, C=N).

Anal. Calcd. for $C_{10}H_{13}NO$: C, 73.61; H, 7.97; N, 8.58. Found: C, 73.39; H, 7.77; N, 8.34.

The **picrate** (from ethyl alcohol) had m.p. 179–180°.

Anal. Calcd. for $C_{16}H_{16}N_4O_8$: C, 48.97; H, 4.08; N, 14.28. Found: C, 48.99; H, 4.25; N, 14.05.

B. From **3-Methyl-3,4,5,6,7,8-hexahydro-2-quinolone** (IIe).—One gram of the hexahydro-2-quinolone was added to cold 96% sulfuric acid and then stirred at room temperature for 3

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(13) R. J. Gillespie and E. A. Robinson, "The Sulfuric Acid Solvent System" in "Advances in Inorganic Chemistry and Radiochemistry," Vol. I, H. J. Emeleus and A. G. Sharpe, Ed., Academic Press, New York, N. Y., 1959.

(14) F. A. Cotton and G. Wilkenson, "Advanced Inorganic Chemistry," Interscience-Wiley, Inc., New York, N. Y., 1962, p. 422.

(15) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovic, and J. Terrell, *J. Am. Chem. Soc.*, **85**, 217 (1963).

(16) All boiling points and melting points are uncorrected, and all infrared spectra were taken in carbon tetrachloride or chloroform.

(17) Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(18) This step was performed in order to remove any polymeric substances and unaromatized material (IIb), which under these conditions were present in only trace amounts. The quantity of IIb that could be isolated *via* this procedure varies with the time of the reaction. The maximum amount was obtained when the keto nitrile was kept at 0–5° in 96% sulfuric acid for 2 hr. and then poured over chipped ice.

hr. The mixture was poured on ice and the aqueous solution extracted with chloroform. Drying and removal of the solvent left a glassy residue. The acidic aqueous solution was neutralized with ammonia and extracted with chloroform. The removal of the solvent left a small amount of solid material. When the residues from both extractions were combined, dissolved in ethyl alcohol, and treated with picric acid, they yielded 0.7 g. of a picrate. This picrate when mixed with that obtained from A did not depress the melting point. The yield of free base was 30%.

3-Methyl-3,4,5,6,7,8-hexahydro-2-quinolone (IIe).—IIe was prepared by treating 2-methyl-3-(2-oxocyclohexyl)propionitrile (Ie) with methanolic potassium hydroxide in *t*-butyl alcohol by a previously described procedure.[5] Yield of material was 40%, m.p. 115–116° (from 1:1 alcohol–water) or sublimation at 90–100° (0.5 mm.). The infrared spectrum exhibited bands at 3.1 and 3.2 (NH, NH assoc.) and 6.0 μ (C=O).

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.72; H, 9.09; N, 8.48. Found: C, 72.99; H, 9.05; N, 8.63.

2-Methyl-3-(2-oxocyclohexyl)propionitrile (Ie).—A solution of 30.2 g. (0.2 mole) of the pyrrolidine enamine[11] of cyclohexanone in 200 ml. of dry dimethylformamide was refluxed for 36 hr. with 24.1 g. (0.36 mole) of α-methacrylonitrile. After the addition of 10 ml. of water, the mixture was refluxed for 1 hr. and then poured into 1 l. of water. The aqueous solution was extracted several times with ether and the combined extracts were washed with 5% hydrochloric acid and then with 5% sodium bicarbonate. The ethereal solution, after drying overnight with magnesium sulfate, was concentrated, and the residue was distilled at 114–115° (0.5 mm.), n^{29}D 1.4625. The product weighed 22 g. (66%) and the infrared spectrum exhibited bands at 4.4 (C≡N) and 5.8 μ (C=O).

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.72; H, 9.09; N, 8.48. Found: C, 72.93; H, 9.10; N, 8.44.

The **semicarbazone** (from ethyl alcohol) had m.p. 164–165°.

Anal. Calcd. for $C_{11}H_{18}N_4O$: C, 59.45; H, 8.10; N, 25.22. Found: C, 59.58; H, 8.35; N, 24.96.

4-Methyl-5,6,7,8-tetrahydro-2-quinolone (IIId). A. From 3-methyl-3-(2-oxocyclohexyl)propionitrile (Id).—The cyano ketone was added in the usual manner to 96% sulfuric acid and, after isolation procedure similar to that of IIIe, gave the 4-methyl derivative in 40% yield, m.p. 240–241° (lit.[7] m.p. 217–218°). The infrared spectrum exhibited the expected quinolone absorption with bands at 3.1 (NH) and 6.05 and 6.20 μ (doublet, C=O, C=N). The n.m.r. spectrum is in good agreement[7] with the other quinolone structures reported herein.

Anal. Calcd. for $C_{10}H_{13}NO$: C, 73.61; H, 7.97; N, 8.58. Found: C, 73.38; H, 8.07; N, 8.58.

B. From 4-methyl-3,4,5,6,7,8-hexahydro-2-quinolone (IId).—A solution of 0.2 g. of the hexahydro derivative in 2.0 ml. of 96% sulfuric acid was stirred for 3 hr. at room temperature. Quenching of the solution in ice–water and neutralization with ammonium hydroxide gave a solid (0.1 g., 50%), which, upon admixing with the product obtained from A above, gave no depression in melting point.

4-Methyl-3,4,5,6,7,8-hexahydro-2-quinolone (IId).—IId was prepared by treating the keto nitrile Id with methanolic potassium hydroxide in *t*-butyl alcohol according to Campbell and Stevens[5] and had m.p. 124–125° (from water). The infrared spectrum exhibited bands at 3.1 and 3.2 (NH, NH assoc.) and 6.0 μ (C=O).

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.72; H, 9.09; N, 8.48. Found: C, 72.92; H, 8.94; N, 8.70.

3-Methyl-3-(2-oxocyclohexyl)propionitrile (Id).—Id was prepared *via* the cyclohexanone enamine and crotonitrile using the procedure described for Ie. The yield was rather low (20%). Id had b.p. 145–147° (0.5 mm.), n^{26}D 1.4710. The infrared spectrum exhibited bands at 4.4 (C≡N) and 5.85 μ (C=O).

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.72; H, 9.09; N, 8.48. Found: C, 72.78; H, 9.08; N, 8.24.

The **semicarbazone** (from ethyl alcohol) had m.p. 179–180°.

Anal. Calcd. for $C_{11}H_{18}N_4O$: C, 59.45; H, 8.10; N, 25.22. Found: C, 59.41; H, 8.23; N, 25.08.

Cyclopentano[*e*]-2-pyridone (IIIa). A. From 2-(2-Cyanoethyl)cyclopentanone (Ia).—To 100 ml. of cold concentrated sulfuric acid was added slowly 13.7 g. (0.1 mole) of the keto nitrile Ia over a 2-hr. period. After stirring in the cold for 3 hr., the mixture was diluted in ice–water. The acid solution was extracted with chloroform and then neutralized with ammonia. The clear solution was extracted repeatedly with chloroform; the combined extracts were dried; the solvent was removed. Recrystallization (ethyl acetate–hexane) of the solid residue (m.p. 82–83°) gave a product which was identified as the corresponding amide (V).[19] The infrared exhibited bands at 5.83 (C=O) and 6.02 μ (C=O, amide). The amide V was heated at 170–180° for 1 hr. and then sublimed *in vacuo* [80–100° (0.2 mm.)] to give pure **cyclopentano[*e*]-3,4-dihydro-2-pyridone (IIa)**, m.p. 114–115°. The infrared spectrum of IIa exhibited bands at 3.1 and 3.2 (NH, NH assoc.) and 6.0 μ (C=O). The ultraviolet maximum (ethyl alcohol) appeared at 246 mμ (ε 5029).

Anal. Calcd. for $C_8H_{11}NO$: C, 70.07; H, 8.02; N, 10.21. Found: C, 69.55; H, 8.00; N, 10.45.

When the dihydro derivative (IIa) was dissolved in cold 96% sulfuric acid (0.5 g. in 4 ml.) and the solution stirred at room temperature for 3 hr., then poured over ice, neutralized with ammonia, and extracted with chloroform, there was obtained 0.35 g. (71%) of the 2-pyridone (IIIa), m.p. 181–182° (lit.[20] m.p. 180–181°). The **picrate** (ethyl alcohol) melted at 160–161° (lit.[8] m.p. 160°).

Cycloheptano[*e*]-2-pyridone (IIIc). A. From 2-(2-cyanoethyl)cycloheptanone (Ic).—A solution of 5.45 g. (0.033 mole) of the keto nitrile[11] in 20 ml. of 96% sulfuric acid was, after mixing in the cold, stirred at room temperature for 3 hr. After dilution with ice–water the mixture was extracted several times with chloroform; the combined extracts were dried (magnesium sulfate) and concentrated. The residue, after recrystallization from aqueous ethyl alcohol (1:1), had m.p. 114–115°; infrared spectrum, 2.89 and 3.05 (NH, NH assoc.) and 6.00 μ (C=O). This product (45%) was identical with the one prepared (15%) by treating the keto nitrile with methanolic potassium hydroxide in *t*-butyl alcohol and, therefore, identified as the 3,4-dihydro-2-pyridone derivative (IIc).

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.72; H, 9.09; N, 8.48. Found: C, 72.56; H, 9.12; N, 8.50.

Neutralization of the acidic aqueous solution after chloroform extraction (above) led to a second precipitated product, which after extraction with chloroform, drying, solvent removal, and sublimation *in vacuo* [140–160° (0.5 mm.)], melted at 199–200°. The yield was 0.2 g. The infrared spectrum exhibited bands at 3.0 (NH) and 6.08 and 6.25 μ (C=O, C=N).

Anal. Calcd. for $C_{10}H_{13}NO$: C, 73.61; H, 7.97; N, 8.58. Found: C, 73.67; H, 7.78; N, 8.72.

B. From the 3,4-Dihydro-2-pyridone (IIc).—One gram of the dihydro-2-pyridone (IIc) in 4 ml. of 96% sulfuric acid was stirred overnight at room temperature. The mixture was poured onto chipped ice and extracted with chloroform. The acid solution was then made alkaline with ammonium hydroxide and the precipitated solid was removed by filtration. Sublimation at 140–160° (0.5 mm.) yielded 0.56 g. (57%) of the 2-pyridone (IIIc).

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(19) N. P. Shusherina, R. Y. Levina, and M. Y. Jure [*Vestnik Moskov. Univ., Ser., Mat., Mekh., Astron., Fiz., Khim.*, **12**, No. 6, 173 (1957); *Chem. Abstr.*, **53**, 2175*d* (1959)] give m.p. 77–78°.

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