4,6-Dihydroxyimidazo[4,5-c]pyridine-2-thiol (XIV).—Sodium (4.5 g.) was dissolved in 180 ml. of absolute ethanol, and then 6.0 g. of 4-acetamide-2-imidazolethione-5-carboxylic acid methyl ester (XII) was added. The solution was refluxed for 15 min. on a steam bath, and then the pH was adjusted to 6 with glacial acetic acid. The mixture was stirred for 30 min. and cooled. The light green solid was filtered, suspended in 75 ml. of distilled water, and stirred an additional 30 min. The crude material was filtered and washed well first with distilled water and then with ethanol. The light green solid was dried at 60° to yield 5.3 g., m.p. > 300°.

Anal. Calcd. for $C_6H_5N_3O_2S \cdot H_2O$: C, 35.8; H, 3.5; N, 20.9. Found: C, 36.0; H, 4.6; N, 20.5.

A sample was dried at 130°.

Anal. Calcd. for $C_6H_5N_3O_2S$: C, 39.3; H, 2.7; N, 22.9. Found: C, 39.3; H, 3.0; N, 22.7.

4,6-Dihydroxyimidazo[4,5-c]pyridine (I).—4-Imidazoleacetamide-5-carboxylic acid methyl ester (XIII, 10.0 g.) was added to 7.5 g. of sodium dissolved in 300 ml. of absolute ethanol. The solution was refluxed on a steam bath for 30 min. and then acidified with glacial acetic acid. The mixture was stirred for 30 min., cooled, and filtered, and the light tan material was suspended in 100 ml. of water, stirred for 30 min., and again filtered. The cyclized product was dried to yield 7.5 g. (91%), m.p. > 300°, and a small sample was recrystallized from glacial acetic acid and dried at 130° for analysis.

Anal. Calcd. for $C_6H_4N_3O_2$: C, 47.7; H, 3.3; N, 27.8. Found: C, 47.6; H, 3.4; N, 28.0.

4-Acetamide-2-chloroimidazole-5-carboxylic Acid Methyl Ester (XVI).—4-Acetic acid-2-chloroimidazole-5-carboxylic acid dimethyl ester (XI, 10 g.) was treated with aqueous ammonia as for the synthesis of XII and X. The solid was recrystallized from methanol–water to give 8.0 g. of product, m.p. 235–237° dec.

Anal. Calcd. for $C_7H_8ClN_3O_3$: C, 38.7; H, 3.7; N, 19.3. Found: C, 38.6; H, 3.3; N, 19.0.

2-Chloro-4,6-dihydroxyimidazo[4,5-c]pyridine (XX).—4-Acetamide-2-chloroimidazole-5-carboxylic acid methyl ester (XVI, 10.0 g.) was added to 7.5 g. of sodium dissolved in 300 ml. of absolute ethanol. This solution was refluxed on a steam bath for 30 min. and then transferred to an erlenmeyer flask. The pH of the solution was adjusted to 6 with glacial acetic acid, and the mixture was stirred for 30 min. and cooled. The light yellow material was filtered, suspended in 100 ml. of distilled water, and stirred for 30 min. The cyclized product was filtered and dried to yield 5.5 g. of light pink solid (65%), m.p. > 300°. A small sample was recrystallized from glacial acetic acid for analysis.

Anal. Calcd. for $C_6H_4ClN_3O_2$: H, 2.2; N, 22.6. Found: H, 2.5; N, 22.7.

4-Imidazoleacetamide-5-carboxylic Acid.—To 50 ml. of 2 *N* sodium hydroxide was added 2 g. of 4-imidazoleacetamide-5-carboxylic acid methyl ester (XIII). The solution was gently refluxed for 45 min. and then acidified with glacial acetic acid and placed in the refrigerator for 12 hr. The crude brown crystals which were filtered weighed 1.2 g. (70.6%). The crude product was reprecipitated from hot dilute sodium hydroxide (30 ml.) with acetic acid, and the white crystals obtained melted at 240° dec. The compound was dried over phosphorus pentoxide at 110° for analysis.

Anal. Calcd. for $C_6H_7N_3O_2$: C, 42.6; H, 4.1; N, 24.8; neut. equiv., 169. Found: C, 42.4; H, 3.9; N, 24.9; neut. equiv., 168.

The Conversion of 3-Aminoalkylidene-2,4-pyrandiones into 4-Pyridones

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Dehydroacetic acid reacts rapidly with primary amines in warm aqueous dimethylformamide to give aminoethylidenepyrandiones. These compounds can be converted into N-substituted 4-pyridones. Proof of structure of the intermediate compounds and the mechanistic pathway of the dehydroacetic acid–pyridone conversion are discussed.

The conversion of dehydroacetic acid (I) into 2,6-dimethyl-4-pyridinol by the action of aqueous ammonia was first described by Haitinger in 1885.[1] When methylamine was used, 1,2,6-trimethyl-4-pyridone was formed in 94% yield.[2]

Two mechanisms have been proposed for the reaction of ammonia with I. The simpler route, as suggested by Brody and Ruby,[3] involves attack by ammonia at the 6-position followed by opening of the pyrone ring and recyclization with the loss of water and carbon dioxide. A more complicated mechanism was proposed earlier by Feist.[4] He postulated that ammonia condensed first with the carbonyl group in the side chain with elimination of water. This step is analogous to the reaction of ammonia with ethyl acetoacetate.[5] The pyrone ring would then be opened (presumably by attack of water) and subsequently closed to the pyridone system. The isolation of 3-(1-iminoethyl)-4-hydroxy-6-methyl-2-pyrone and its conversion into 2,6-dimethyl-4-pyridinol[6a,b] would lend support to the latter theory.

We have synthesized several N-substituted 4-pyridones (Table III) using dehydro acids and primary amines as starting materials. The rearrangement of the intermediate compounds (Table II) was studied in detail. Phenethylamine and dehydroacetic acid were heated in 50% aqueous dimethylformamide for 30 minutes. A nonbasic compound, whose analysis indicated condensation with loss of one molecule of water, was obtained in 70% yield. A minor product, isolated in 5% yield, was shown to be 1-phenethyl-2,6-dimethyl-4-pyridone (IV) by an unequivocal synthesis in which 2,6-dimethyl-4-pyrone (V) was used as starting material.[7,8]

The ultraviolet spectrum of the major product shows maxima at 237 and 314 mμ while the pyridone IV has a single maximum at 266 mμ. The course of the

(1) L. Haitinger, *Ber.*, **18**, 452 (1885).

(2) S. Hünig and G. Kobrich *Ann.*, **617**, 181 (1958).

(3) F. Brody and P. R. Ruby, "Pyridine and Derivatives," Part 1, E. Klingsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 186.

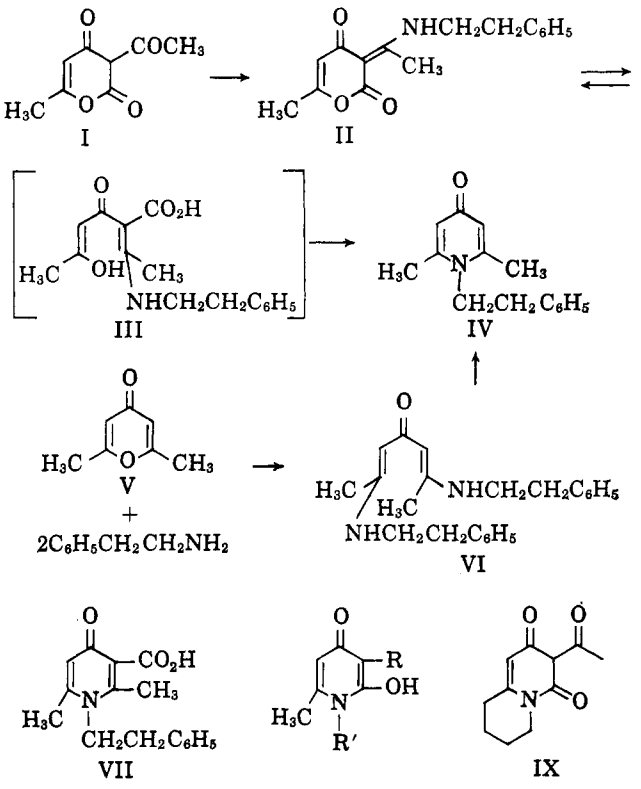
(4) F. Feist, *Ann.*, **257**, 253 (1890).

(5) R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 106.

(6) (a) S. Iguchi, K. Hisatsune, M. Himeno, and S. Muraoka, *Chem. Pharm. Bull.* (Tokyo), **7**, 323 (1959). (b) NOTE ADDED AUGUST 7, 1963: S. Garratt, *J. Org. Chem.*, **28**, 1886 (1963), reported the conversion of 3-(α-methylamino)ethylidene-6-methylpyran-2,4-dione into N-methyllutidone by the action of methylamine. In this case, bis-2,7-methylaminohepta-2,5-dien-4-one was isolated as an intermediate.

(7) R. T. Conley, E. Nowoswiat, and W. G. Reid, *Chem. Ind.* (London), 1157 (1959).

(8) R. T. Conley, E. Nowoswiat, and E. Kosak, Abstract of Papers, 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960, p. 13-O. We wish to thank Dr. Conley for a private communication in which he described the experimental conditions for ring closure of bis(aminovinyl) ketones.



VIIIa, R = alkyl or acetyl; R′ = H
b, R = acetyl; R′ = $CH_2CH_2C_6H_5$

reaction was followed by measuring the ultraviolet spectrum of the solid material isolated periodically from an aliquot of reaction solution (Table I). The results show that the intermediate compound is formed rapidly and is converted slowly into IV.

TABLE I

REACTION OF DEHYDROACETIC ACID WITH PHENETHYLAMINE IN DIMETHYLFORMAMIDE–WATER (1:1) AT 105°

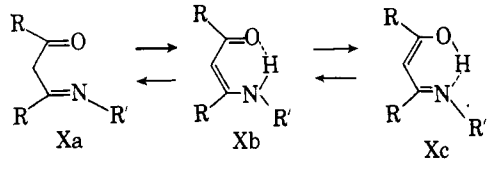
Time	λ_{max}^{MeOH}, mμ			ϵ_{max}		
30 min.	237		314	21,300		22,700
90 min.	237	266	314	18,400	8,900	18,900
3 hr.	237	266	314	11,300	9,600	11,300
6 hr.		266	314		19,800	8,600
12 hr.		266			20,900	

Structures II, VII, and VIIIb were regarded as possibilities for the intermediate compound. The insolubility of the intermediate in sodium bicarbonate and hydroxide solution definitely excludes structure VII. Although 2,6-dimethyl-4-hydroxy-3-pyridinecarboxylic acid was the major product formed in the reaction of ammonia with dehydroacetic acid at temperatures below 100°,[9] we have never been able to isolate pyridonecarboxylic acids in our work with primary amines. In one attempt to synthesize this type of compound, 2,6-dimethyl-4-oxo-3-pyrancarboxylic acid[10] was treated with a solution of phenethylamine in aqueous dimethylformamide at steam bath temperature. Rapid decarboxylation took place under these conditions; compound IV was the only product isolated.

Ketene reacts with pyridine to give a compound of rather complex structure. One of the degradation products (IX) as well as simpler models (VIIIa) were studied by Berson and co-workers.[11,12] A hypsochromic shift of the highest absorption band occurs when the ultraviolet spectra of these compounds are measured in basic solution. The compounds are soluble in sodium hydroxide solution, give positive ferric chloride tests and form 2,4-dinitrophenylhydrazone derivatives. Since none of these properties were shown by the intermediate we isolated, structure VIIIb also may be rejected.

Evidence for structure II was obtained by degradation of the intermediate to sodium dehydroacetate and phenethylamine in the presence of hot alcoholic sodium carbonate solution. The infrared spectrum (chloroform) of II showed strong bands at 1700 (lactone C=O), 1660, 1610, and 1580 $cm.^{-1}$. There was no OH or NH absorption in the normal frequency range in either the infrared or near infrared spectrum; however, strong hydrogen bonding or chelation effects would be expected in this type of compound.[13]

The nuclear magnetic resonance spectra of a number of compounds obtained from the condensation of β-diketones with primary amines have been studied.[14] Of the three tautomeric possibilities (Xa, Xb, or Xc), the compounds were shown to exist predominantly in the ketamine form Xb. Confirmatory evidence for the ketamine structure in the case of the intermediates reported in this paper was provided by the n.m.r. spectrum (deuteriochloroform) of compound XI. The data obtained was quite similar to that reported by Dudek and Holm. The significant feature of the spectrum was a doublet centered at 5.37 τ (J = 6.0 c.p.s.). This indicates splitting of the $N-CH_2$ signal by a hydrogen attached to the nitrogen atom.



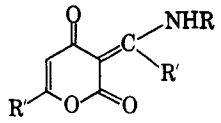
The pathway from compound II to the pyridone ring system most likely involves the open chain intermediate III; however, this part of the mechanism has not been proved conclusively. The dependence upon water for the conversion of II to IV was demonstrated by heating a solution of the ketamine in purified dimethylformamide. At the end of four hours, the ultraviolet spectrum of the recovered solid product did not show the typical 4-pyridone absorption at 266 mμ.

Subtle steric factors apparently play a part in the transformation of the ketamine intermediates into 4-pyridones. This was evident from the fact that α-methylphenethylamine and dehydroacetic acid gave XII as the sole product after twelve hours under the usual reaction conditions (see Table I). Formation of the pyridone XVI in this case required treatment with warm mineral acid. Analogy for this rearrangement is found in the acid-catalyzed conversion of α-anilinomethylene δ-lactones into cyclic enamines.[15] We sug-

(9) J. N. Collie, *J. Chem. Soc.*, **77**, 971 (1900).
(10) J. N. Collie and T. P. Hilditch, *ibid.*, 787 (1907).
(11) J. A. Berson, W. M. Jones, and L. F. O'Callaghan, *J. Am. Chem. Soc.*, **78**, 622 (1956).
(12) J. A. Berson and W. M. Jones, *ibid.*, **78**, 1625 (1956).
(13) N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank, and D. J. Wallace, *ibid.*, **71**, 3337 (1949).
(14) G. O. Dudek and R. H. Holm, *ibid.*, **84**, 2691 (1962).
(15) F. Korte, *Angew. Chem. Intern. Ed. Engl.*, **1**, 61 (1962).

TABLE II

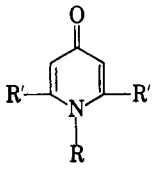
AMINOALKYLIDENEPYRANDIONES

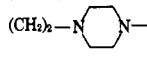
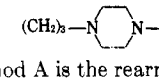


Compd.	R	R′	Yield, %	M.p., °C.	Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
II	$CH_2CH_2C_6H_5$	CH_3	70	90–91	$C_{16}H_{17}NO_3$	70.85	6.28	5.17	71.06	6.19	5.27
XI	$CH_2C_6H_5$	CH_3	69	80–81	$C_{15}H_{15}NO_3$	70.04	5.84	5.45	70.11	5.99	5.37
XII	$CHCH_3CH_2C_6H_5$	CH_3	70	84–85	$C_{17}H_{19}NO_3$	71.58	6.66	4.91	71.52	6.37	4.91
XIII	$(CH_2)_3N(CH_3)_2$	C_6H_5	27	120–121	$C_{23}H_{24}N_2O_3$	73.40	6.39	7.45	73.69	6.53	7.47
XIV	$CH_2CH_2C_6H_5$	C_6H_5	34	146–147	$C_{26}H_{21}NO_3$	78.99	5.32	3.54	78.99	5.31	3.60
XV	β-(3-Indolyl)ethyl	CH_3	80	196–198	$C_{18}H_{18}N_2O_3$	69.68	5.81	9.03	69.29	6.17	9.12

TABLE III

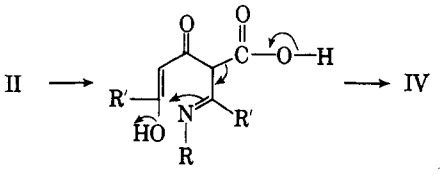
4-PYRIDONES



Compd.	R	R′	Method[a]	Yield, %	M.p., °C.	Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
IV	$CH_2CH_2C_6H_5$	CH_3	A	25	164–166	$C_{15}H_{17}NO$	79.30	7.50	6.17	79.20	7.76	6.23
XVI	$CHCH_3CH_2C_6H_5$	CH_3	A	31	235–236	$C_{16}H_{19}NO\cdot HCl$	69.06	7.20	12.77[b]	69.04	7.57	12.71[b]
XVII	$CH_2CH_2C_6H_5$	C_6H_5	A	48	247–252[c]	$C_{25}H_{21}NO$	85.47	5.98	3.99	85.50	6.05	3.77
XVIII	β-(3-Indolyl)ethyl	CH_3	A	79	281–282	$C_{17}H_{18}N_2O$	76.69	6.77	10.53	75.87	6.66	10.60
XIX	$(CH_2)_3N(CH_3)_2$	CH_3	B	70	123–125	$C_{12}H_{20}N_2O$	69.3	9.62	13.46	69.8	9.66	13.38
XX	$(CH_2)_3OH$	CH_3	B	74	188–189	$C_{10}H_{15}NO_2$			7.73			7.88
XXI		CH_3	B	48	157–158	$C_{19}H_{25}N_3O$			13.50			13.42
XXII		CH_3	B	50	144–145	$C_{20}H_{27}N_3O$			12.92			12.67

[a] Method A is the rearrangement of the corresponding pyrandione by heating in dilute sulfuric acid–methanol. Method B is heating a mixture of dehydroacid and amine in water or aqueous dimethylformamide for 6 hr. [b] Chloride ion by titration. [c] Lit. m.p. 258°, M. J. Chauvelier, *Bull. soc. chim. France*, 734 (1954).

gest structure XXIII as an intermediate for the conversion of aminoalkylidene pyrandiones into 4-pyridones in acidic media. In such a species, there should be less crowding in the transition state for ring closure than in structure III; decarboxylation and ring closure would probably occur in concerted fashion.



XXIII

Some hydrolytic cleavage of the aminoalkylidenepyrandione to dehydro acid and primary amine took place during rearrangement in acid. This side reaction was especially serious when R′ = phenyl. At first it was thought that this cleavage represented an alternative pathway for pyridone formation from the intermediate compounds. To test this idea, an equimolar mixture of dehydroacetic acid and phenethylamine was subjected to the conditions of the acid-catalyzed rearrangement. No 4-pyridone was formed; the only solid product isolated was 2,6-dimethyl-4-pyrone, a product of rearrangement of dehydroacetic acid. Therefore, the 4-pyridones formed in the acid-catalyzed rearrangement of aminoalkylidenepyrandiones must be derived from an open-chain species such as XXIII.

Experimental[16]

General Procedure for Synthesis of Aminoalkylidenepyrandiones.—Equimolar quantities of the dehydro acid and primary amine are dissolved in 50% aqueous dimethylformamide. The solution is heated under reflux *ca.* 30 min. in the case of the simpler amines. When higher molecular weight amines or dehydrobenzoylacetic acid are used, a dimethylformamide solution is heated under reflux for 6 hr. The solvents are distilled *in vacuo* and the residual oil is stirred with ether to cause solidification. The crude product may be purified by recrystallization from benzene–hexane or ether–benzene.

3-(1-Phenethylamino)ethylidene-6-methyl-3*H*-pyran-2,4-dione (II).—A solution of 16.8 g. (0.10 mole) of dehydroacetic acid and 12.1 g. (0.10 mole) of phenethylamine in 60 ml. of 50% dimethylformamide was heated under reflux for 30 min. The solvent was distilled *in vacuo* and the residue was treated with ether to produce a solid material. The crude product was stirred for 15 min. in 100 ml. of cold 10% hydrochloric acid, then filtered to give 19.0 g. (70%) of ivory-colored crystals, m.p. 88–89°. An analytical sample of 3-(1-phenethylamino)ethylidene-6-methyl-3*H*-pyran-2,4-dione (II) was prepared by recrystallization from benzene–ether, m.p. 90–91°; λ_{max}^{MEOH} 237, 314 mμ (ε 20,600; 22,200). The infrared spectrum (chloroform) showed strong bands at 1700 (lactone C=O), 1660, 1610, and 1580 cm.$^{-1}$.

(16) Melting points were taken in open capillaries and are corrected. Infrared spectra were determined with a Perkin-Elmer Infracord Model 137 spectrophotometer; ultraviolet spectra were measured with a Warren Spectracord. The n.m.r. spectrum was determined at 60 Mc. with a Varian, Model HR-60, spectrometer.

The compound was insoluble in dilute sodium hydroxide solution, and the ferric chloride test was negative. The iodoform test was also negative and no dinitrophenylhydrazone formed.

The acid filtrate from the previous experiment described was made basic and extracted with chloroform. Drying and concentration *in vacuo* gave 1.05 g. (4.6%) of 1-phenethyl-2,6-dimethyl-4-pyridone, m.p. 164–167°.

2,6-Diphenethylamino-2,5-heptadien-4-one (VI).—A solution of 6.0 g. (0.049 mole) of 2,6-dimethyl-4-pyrone in 50 ml. of water was treated with 11.7 g. (0.097 mole) of phenethylamine. The solution was heated at 90° for 30 min. and cooled. The solid material which formed was collected and recrystallized from benzene–ether to give 4.8 g. (29%) of light yellow crystals, m.p. 114–115°; λ_{max}^{MeOH} 380 mμ (ε 47,400); $\nu_{max}^{CHCl_3}$ 1695, 1590, 1540 (sh), and 1315 cm.$^{-1}$.

Anal. Calcd. for $C_{28}H_{28}N_2O$: C, 79.31; H, 8.05; N, 8.05. Found: C, 79.46; H, 7.96; N, 8.18.

1-Phenethyl-2,6-dimethyl-4-pyridone (IV).—A mixture of 3.80 g. (0.011 mole) of the bis(aminovinyl) ketone (VI) and 50 ml. of water was steam distilled over a 6-hr. period. The distillate was concentrated *in vacuo*, the residue was dissolved in methanol–ether and converted to the hydrochloride (1.26 g., m.p. 257–259°). The free base was regenerated and extracted into chloroform. Drying and concentration *in vacuo* gave a white solid which was stirred in ether and collected; yield, 0.78 g.; m.p. 168–170°. A mixture melting point with 1-phenethyl-2,6-dimethyl-4-pyridone prepared by acid-catalyzed rearrangement of compound II was not depressed.

Conversion of 3-(1-Phenethylamino)ethylidene-6-methyl-3*H*-pyran-2,4-dione (II) into 1-Phenethyl-2,6-dimethyl-4-pyridone (IV).—A solution of 24.0 g. (0.089 mole) of the pyrandione in 200 ml. of methanol and 100 ml. of 30% sulfuric acid was heated under reflux for 1 day. The solution was diluted with 100 ml. of water, and the methanol was distilled. The aqueous solution was made alkaline and extracted with chloroform. Drying and concentration *in vacuo* gave 13.5 g. of yellow solid. Recrystallization from aqueous methanol gave 5.0 g. of white crystalline product, m.p. 168–169°. A further recrystallization gave the analytical sample, m.p. 164–166°; λ_{max}^{MeOH} 266 mμ (ε 20,000); $\nu_{max}^{CHCl_3}$ 1640 and 1560 cm.$^{-1}$.

The identity of the compound with that obtained from dehydroacetic acid and phenethylamine after 12-hr. heating in 50% dimethylformamide was established by spectroscopic and mixture melting point determinations.

2,6-Dimethyl-4-oxo-3-pyrancarboxylic Acid.—A modified procedure of Collie and Hilditch[10] was used. A 10-g. sample of dehydroacetic acid was heated in the presence of 35 ml. of 85% sulfuric acid at 95–100° for 30 min. The orange-colored solution was poured onto 200 g. of ice. The solid which formed was filtered and washed with water to give 1.7 g. of the desired pyrancarboxylic acid, m.p. 97–99° (lit.[10] m.p. 98.5–99°); mixture melting point with dehydroacetic acid was depressed to 80–90°.

Reaction of 2,6-Dimethyl-4-oxo-3-pyrancarboxylic Acid with Phenethylamine.—A solution of 0.70 g. (5.7 mmoles) of phenethylamine and 0.96 g. (5.7 mmoles) of 2,6-dimethyl-4-oxo-3-pyrancarboxylic acid in 25 ml. of 50% dimethylformamide was heated on the steam bath for 90 min. During the first few minutes a brisk evolution of gas was noticed. The solvents were concentrated *in vacuo* and the residue was triturated with ether. The light yellow solid obtained (0.47 g.) had m.p. 150–160°. Recrystallization from benzene–ether gave material with m.p. 159–163°; mixture melting point with 1-phenethyl-2,6-dimethyl-4-pyridone was not depressed.

Basic Cleavage of 3-(1-Phenethylamino)ethylidene-6-methyl-3*H*-pyran-2,4-dione.—A mixture of 0.56 g. (2.1 mmoles) of compound II, 10 ml. of 10% sodium carbonate solution, and enough methanol to give a clear solution was heated under reflux for 2 hr. The methanol was distilled *in vacuo* and cold dilute hydrochloric acid was added to the aqueous solution until pH 4 was attained. The precipitated material was collected and washed with cold water; yield, 0.18 g.; m.p. 108–110°; a mixture melting point with dehydroacetic acid showed no depression.

Behavior of Compound II when Heated under Anhydrous Conditions.—A solution of 1.88 g. of 3-(1-phenethylamino)-ethylidene-6-methyl-3*H*-pyran-2,4-dione (II) in 25 ml. of dried and distilled dimethylformamide was heated at 103° for 4 hr. The absence of the 266-mμ band in the ultraviolet spectrum of the recovered solid indicated that no 4-pyridione formed. There was recovered 1.51 g. (80%) of starting material, m.p. 89–90°.

Hydrolysis of 3-(1-Phenethylamino)ethylidene-6-methyl-3*H*-pyran-2,4-dione in Acidic Medium.—A solution of 6.78 g. (0.025 mole) of compound II in 40 ml. of methanol, 20 ml. of water, and 7 ml. of concentrated sulfuric acid was heated under reflux for 2 hr. The solution was concentrated to a small volume; the solid material which formed at this point was collected and treated with cold dilute sodium hydroxide solution. A chloroform extract yielded 1.69 g. of 1-phenethyl-2,6-dimethyl-4-pyridone (IV). The basic aqueous extract was acidified with hydrochloric acid to give 1.01 g. of dehydroacetic acid.

Attempted Formation of 1-Phenethyl-2,6-dimethyl-4-pyridone from Dehydroacetic Acid and Phenethylamine in Acidic Medium.—To a solution of 16.8 g. (0.10 mole) of dehydroacetic acid in 200 ml. of methanol and 100 ml. of 30% sulfuric acid (by volume) was added 12.1 g. (0.10 mole) of phenethylamine. The solution was heated under reflux for 1 day. The methanol was removed by distillation and the acidic aqueous solution was extracted with benzene. The organic extract was concentrated to produce 1.7 g. of dehydroacetic acid, m.p. 109–111°. The aqueous layer was made alkaline and extracted with chloroform. Concentration of the dried extract gave 7.7 g. of acid-soluble material, m.p. 130–140°. Recrystallization from benzene–ether gave 3.6 g. of white crystalline compound, m.p. 134–135°; mixture melting point with 2,6-dimethyl-4-pyrone showed no depression.

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