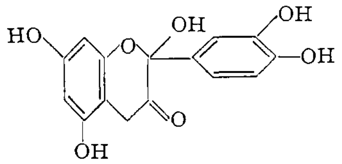
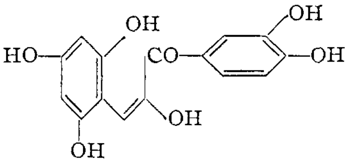
this value of K_m suggests that the reaction was probably competitively inhibited by a split product,[12] *e.g.*, glucose. Glucose was indeed found to be a competitive inhibitor of the enzyme as illustrated by the data presented in the upper plot of Fig. 2. A K_i, *i.e.*, inhibitor–enzyme dissociation constant, of 1.25×10^{-3} *M* was evaluated.

These results indicate that the over-all decolorization process is adequately described by equation 1. This formulation is also consistent with the chemical properties of the decolorized solution.

In aqueous solution at *p*H 3.95, chrysanthemin exists as an equilibrium mixture of I and III.[9] Form I is responsible for the characteristic color of the solution and form III can be recognized by its instantaneous conversion to I when the *p*H of the medium is lowered to <1. By analogy, in the enzyme decolorized solution, the presence of II is shown by the residual color. The existence of IV is demonstrated by the fact that upon acidification, an instantaneous, small but always reproducible, increase in absorbancy is noticeable. The slow intensification of color which follows[3] indicates transformation of the colorless form C, which is the predominate molecular species present, into IV and II. Structure V, *i.e.*, the ketonic tautomer of IV, is suggested as most likely for C for two reasons. In the first place, the heterocyclic ring in IV is no longer resonance stabilized, so that isomerization of the enolic group into the more stable keto form V would be expected to occur.[13] Secondly, open chain tautomers such as the chalcone derivative VI may be ruled out, since careful spectrophotometric examination of enzyme decolorized solutions failed to detect any absorption maximum other than that at 510 mμ and C must be regarded as a colorless product. Either chalcone (VI) or the isomeric diketo form would be expected to exhibit a pronounced yellow color.[14] Destruction of C in air, as reflected in losses in the amount of B, *i.e.*, intensity of color, which could be regenerated by acidification of the decolorized solution, has already been noted.[3] This loss was entirely eliminated when decolorization reactions were carried out in an atmosphere of nitrogen. Autoxidation of C is, however, too slow to have a measurable effect on the kinetics of decolorization observed under the conditions reported in this communication.



V



VI

Acknowledgment.—The author wishes to express his thanks to Mr. Gerard Weiser for technical assistance and to Dr. C. V. Smythe for his interest and encouragement.

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[12] H. T. Huang and C. Niemann, THIS JOURNAL, **73**, 1541 (1951).

[13] G. W. Wheland, "Advanced Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 589–596.

[14] An acyclic 1,2-diketone, *e.g.*, biacetyl, is markedly yellow. Chalcone itself is lightly yellow, but a hydroxylated chalcone, *e.g.*, butein is more deeply colored. Butein derivatives, in fact, occur as pigments in nature: T. A. Geissman, THIS JOURNAL, **63**, 2689 (1941), and M. Shimokoriyama and S. Hattori, *ibid.*, **75**, 1900 (1953).

PHILADELPHIA, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF ARTS AND SCIENCES, UNIVERSITY OF LOUISVILLE]

2-Pyrones. XVIII. 5-Aroyl-2-pyrones and 5-Aroyl-2-pyridones

BY RICHARD H. WILEY AND S. C. SLAYMAKER

RECEIVED NOVEMBER 25, 1955

A series of 5-aroyl-2-pyrones I have been prepared by Friedel–Crafts condensations with coumalyl chloride in 20–93% yield and converted to pyridones (II, III, IV) by reaction with ammonia, amines and hydrazines. *para*-Substitution in the aryl nucleus has been established by degradative and spectral data. Pyridone formation is facilitated by the 5-aroyl substitution. The N-aminopyridone IV is converted to the pyridone by nitrous acid. Unique structural features were observed with the analogous N-anilino derivative IV and the hydroxylamine derivative VI. Peroxide–acetic acid oxidation of 5-benzoyl-2-pyridone gives the benzoyloxy derivative V. Infrared and ultraviolet absorption data for all of these compounds are analyzed.

The description[1] of the first known ketone in the 2-pyrone series has initiated a further study of this class of compounds. A variety of such ketones are now available and we wish to report the results of our studies on the preparation, structure, absorption characteristics and reactions of these ketones and the 2-pyridones derived from them.

5-Aroyl-2-pyrones I are readily available from the aluminum chloride catalyzed reaction of coumalyl chloride with those benzenoid compounds which are liquid and can be used in excess as solvents for the reaction. Using such techniques yields of 73–93% of 5-aroyl-2-pyrones have been obtained from benzene, toluene, bromobenzene and chlorobenzene. Substitution in the *para* position is established by oxidation of the tolyl derivative to *p*-toluic acid. With other benzenoid compounds, apparently because they are less stable to aluminum chloride, poor yields are obtained. Thus, ethylbenzene gives but 20% of product and *m*-xylene and anisole give no ketone at all by this process. Furthermore, the reaction is limited to coumalyl chlo-

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[1] R. H. Wiley and L. H. Knabeschuh, THIS JOURNAL, **77**, 1615 (1955).

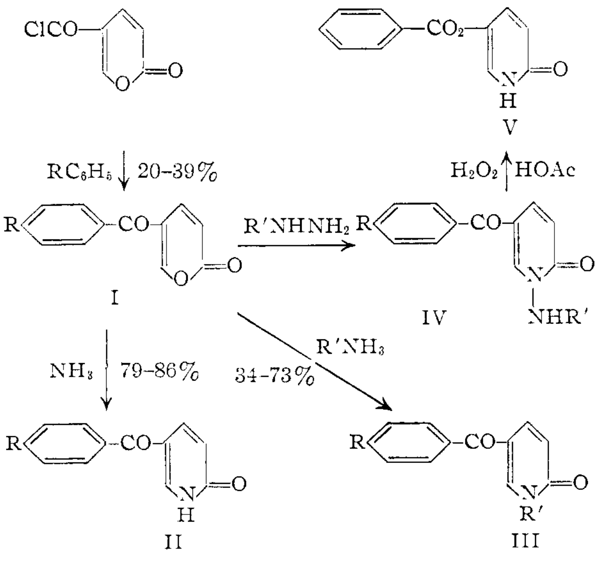
TABLE I

5-AROYL-2-PYRONES

R of formula I	M.p., °C.	Yield, %	Re-cryst. from[a]	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Absorption data Ultra-violet[b]	Infrared[c]					
H	114.5–115	93	BP	71.99	72.02	4.03	3.96	259(4.12)	5.68s	6.11s	6.26m 6.35m	6.45m	8.08s	13.3s 14.3s
CH_3	134–135	73	EW	72.89	72.66	4.71	4.75	265(4.19)	5.70s	6.11s	6.21m	6.43m	8.04s	11.9s
C_2H_5	96.5–97.5	20	CP	73.67	73.48	5.30	5.32	267(4.26)	5.69s	6.13s	6.22m	6.43m	8.08s	12.04s
Br	133–134	81	BP	51.64	51.71	2.53	2.86[d]	268(4.17)	5.70s	6.04s 6.16m	6.29s	6.43m	8.08s	12.01s
Cl	120–121	91	BP	61.43	61.29	3.01	2.98[e]	270(4.27)	5.67s	6.04s 6.16m	6.28s	6.43m	8.06s	11.82s
CH_3O	153–154.5	10	E	67.83	67.94	4.35	4.31	290(4.28) 226(3.85)	5.73s	6.14s	6.24s 6.37m	6.47sh	7.91s 8.04s	11.8s

[a] BP, benzene–petroleum ether; EW, ethanol–water; CP, chloroform–petroleum ether; E, ethanol. [b] Maximum in mμ; log extinction coefficient in parentheses. Ethanol solutions. [c] Principal absorption bands in μ for potassium bromide pellets unless otherwise noted; s, strong; vs, very strong; m, medium; w, weak; sh, shoulder; b, broad. [d] Calcd.: Br, 28.63. Found: Br, 28.64. [e] Calcd.: Cl, 15.18. Found: Cl, 15.21.

ride and cannot be extended to the structurally related isodehydroacetyl chloride presumably because the two methyl groups in *ortho* positions to the carboxyl function inhibit the reaction. All of the 5-aroyl-2-pyrones show a single broad absorption band in the 259–270 mμ region (log ε, 4.12–4.27) except the *p*-methoxyphenyl analog in which this band is shifted to 290 mμ and a second maximum appears at 226 mμ. The infrared data for the aroyl-2-pyrones show absorption bands at 5.68–5.73 μ attributable to the unsaturated lactone (2-pyrone) carbonyl; at 6.04–6.11 μ attributable to the ketone carbonyl and possibly overlapping carbon–carbon double bond absorption; at 6.24–6.37 μ characteristic of phenyl groups; and at 6.43–6.47 μ attributable to carbon–carbon double bond structure of 2-pyrones. Analysis of the infrared absorption data for many 2-pyrones has disclosed[2] that two bands almost invariably appear in the carbon–carbon double bond region 6.0–6.5 μ of 2-pyrones and that they are usually separated by 0.30 μ. In some of these ketones there is a clear differentiation of bands attributable to C=O and C=C, at 6.04 and 6.16 μ, respectively, with a second C=C absorption appearing at 6.43 μ, a difference of 0.28 μ. All but the benzoyl compound show absorption bands near 12.0 μ characteristic of *p*-substituted phenyl group. The data are summarized in Table I.



All of the 5-aroyl-2-pyrones gave 5-aroyl-2-pyridones II, a previously unknown class of compounds, with ease. The 2-pyridones are soluble in alkali and give negative ferric chloride tests as do other 2-pyridones with electron attracting groups in the 5-position.[3] The sodium salt of 5-benzoyl-2-pyridone and the 3-bromo derivatives of 5-benzoyl-2-pyridone and its N-methyl derivative have been isolated and characterized. 5-Benzoyl-2-pyridone has been alkylated in potassium hydroxide solution with dimethylaminoethyl chloride to give N-dimethylaminoethyl-5-benzoyl-2-pyridone. Although the analytical data for the halobenzoylpyridones is not completely satisfactory for some of the elements the crystalline appearance indicates substantial purity and the absorption data removes any serious question as to their constitution. Oxidation of 5-(*p*-chlorobenzoyl)-2-pyridone gives *p*-chlorobenzoic acid. The 5-aroyl-2-pyridones show two absorption maxima in the ultraviolet, occurring at 251–265 mμ (log ε 3.83–4.16) and at 291–293 mμ (log ε 4.14–4.37). Although these two absorption bands occur at about the same wave lengths at which absorption is observed with other 2-pyridones[1] the intensity is reversed which suggests that alternative structural correlations exist. The absorption at 251–265 mμ corresponds to that observed at 245.5–258.5 mμ (log ε 3.99–4.24) in acetophenone and its *para* substituted derivatives[4] as well as to the first of the two bands observed in 2-pyridones. A comparison with data for the 2-pyridones shows that the first absorption band which appears at 229 mμ (log ε 3.85) in 2-pyridone shifts to longer wave lengths when an electron attracting group is substituted in the 5-position. Thus, in 6-methyl-5-carboxy-2-pyridone the absorption is at 261 mμ (log ε 4.14) and in one cyclic 5-acyl-2-pyridone is at 273 mμ.[5] The other absorption band in 2-pyridones remains at about 300 mμ in this series of compounds. In the 5-aroyl-2-pyridones it appears likely that the two 2-pyridone absorption bands overlap to give a broad absorption in the 290 mμ region and that the lower intensity absorption at 251–265 mμ is due to the aroyl ketone structure.

The infrared spectra of 2-pyridones have been

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[2] Unpublished work with E. V. Mochel.

[3] F. Ramirez and A. P. Paul, THIS JOURNAL, **77**, 1035 (1955).

[4] L. Doub and J. M. Vandenbelt, *ibid.*, **69**, 2714 (1947).

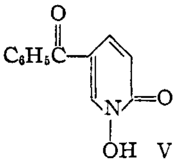
[5] F. Ramirez and A. P. Paul, *J. Org. Chem.*, **19**, 183 (1954).

considered before but not in detail. Solution spectra of 2-pyridones indicate that a strong and characteristic band occurs near 6.05 μ. A second band usually much weaker and probably an absorption due to a C=C stretching frequency is often noted near 6.20 μ.[5] The 5-aroyl-2-pyridones are characterized by absorption at 3.2–4.0 μ (broad), attributable to the N–H and O–H stretching frequencies in tautomeric imide–amide structure perhaps indicative of intramolecular hydrogen bonding; at 6.01–6.03 μ (strong), attributable to the ketone carbonyl in this case; and at 6.14–6.15 μ (very strong), characteristic of the pyridone carbonyl. These data were determined using potassium bromide pellets. Measurements in solution show that the band at 6.15 μ is shifted to 6.08–6.10 μ.

A number of N-alkyl- and N-alkaryl-2-pyridones III have been prepared from various amines. These compounds, as do the unsubstituted-2-pyridones, show the characteristic double absorption maxima in the ultraviolet range at 248–263 mμ (log ε 3.74–4.11) and at 290–294 mμ (log ε 4.04–4.23). The infrared spectra show characteristic absorption bands at 5.97–6.02 μ and at 6.11–6.15 μ attributable to ketone and pyridone carbonyl, respectively. They also show a medium strength band at 6.47–6.54 μ which has been noted before as of general occurrence in N-substituted-2-pyridones.[6] There is no broad absorption in the 3.0–4.0 μ region substantiating the correlation mentioned above between the occurrence of absorption in this region and the imide–amide N–H and O–H bonds in the unsubstituted 2-pyridones.

The reactions of 5-benzoyl-2-pyrone with hydrazine or phenylhydrazine and of 5-*p*-toluyl-2-pyrone with phenylhydrazine give crystalline derivatives with N-amino or N-anilino substituents. N-Amino-5-benzoyl-2-pyridone reacts with nitrous acid to give 5-benzoyl-2-pyridone. The ultraviolet absorption characteristics of this compound, with maxima at 247 and 295 mμ, and the infrared absorption bands at 3.04 μ (N–H stretching); 6.00 μ (ketone carbonyl); 6.14 μ (pyridone carbonyl); and 6.50 μ (N-substitution) are unmistakably similar to those of N-substituted-2-pyridones. The broad absorption band at 3.0–4.0 μ is missing. The analytical data establish a similar structure for the N-aniline derivatives. Base insolubility and failure to undergo conversion to 2-pyridones indicates absence of the 2-pyrone ring. The ultraviolet absorption spectra show maxima at 288 mμ (log ε 4.33) only for the phenyl analog and, for the tolyl analog, at 290 mμ (log ε 4.25) and 272 mμ (log ε 4.31). The maxima at 290 mμ is consistent with the N-anilino-2-pyridone structure but the absence of the maxima in the 250–260 mμ region is not. Furthermore, the infrared absorption characteristics of these two N-anilino-2-pyridones show little resemblance to those of the N-amino-2-pyridone and other 2-pyridones. There is a strong carbonyl band at 5.93 μ and four strong bands between 6.1 and 7.2 μ. The strongest band of the spectra is at 8.1 μ at a position where there is no absorption at all in other 2-pyridones. There is also a broad band in the 3.0–4.0 μ region. It seems adequate at the moment to assign these spectral abnormalities to unique structural factors in view of the chemical data consistent with the N-anilino formulation.

5-Benzoyl-2-pyrone reacts with hydroxylamine to give a crystalline solid which cannot be the oxime of the ketone carbonyl. It is unaffected by ammonia and strong base indicating absence of the 2-pyrone ring. It is distinctly acid having a neutral equivalent of 217 and a pK_a value of 5.13. It has previously been shown[7] that the pH values of oximes are in the 6.89–6.54 range. The compound adds bromine, is oxidized to benzoic acid, does not form an insoluble copper salt, and gives a negative ferric chloride test. By analogy with the hydrazine reaction the most obvious structural possibility for this compound is that of N-hydroxy-5-benzoyl-2-pyridone (VI). The possibility that the recyclization after cleavage by the hydroxylamine resulted in an isoxazole (VII) is eliminated because isoxazoles having no 3-substituent are irreversibly isomerized to β-ketonitriles by alkali whereas the product is actually reprecipitated unchanged from alkaline solution. The negative ferric chloride test and failure to precipitate a copper salt are at variance with the observed behavior of many N-hydroxy-2-pyridones.[8] Studies of the ultraviolet absorption characteristics of N-hydroxy-2-pyridones have established a similarity with the N–H 2-pyridones although no compounds with electron-attracting substituents have been included in these studies. Our hydroxylamine derivative shows a maxima at 290 mμ (log ε 4.22) characteristic of the related 5-benzoyl-2-pyrone and another at 228 mμ (log ε 4.13). There is no indication of the maximum at 250 mμ observed in 5-benzoyl-2-pyrone. This indicates, perhaps, that structural conditions exist where the absorption characteristics of the two types are not as nearly identical as the previous studies seem to indicate. The infrared absorption data are consistent with the N-hydroxy-2-pyridone structure. It has been shown[9] in the only previously recorded case that N-hydroxy substitution does not affect the characteristic 2-pyridone band at 6.1 μ. Our 5-benzoyl compound shows a strong absorption band at 6.15 μ as well as strong absorption at 5.98 μ characteristic of the ketone carbonyl and strong absorption in the 3.0–4.0 μ range probably associated with an N-hydroxy-2-pyridone/2-hydroxypyridine-N-oxide tautomerism. Attempts to synthesize this compound by the hydrogen peroxide–glacial acetic acid oxidation of 5-benzoyl-2-pyridone, a technique previously shown to be successful in such reactions,[10] resulted in the forma-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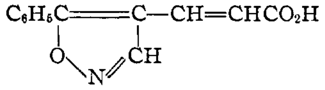
VII

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(6) F. Ramirez and A. P. Paul, THIS JOURNAL, **77**, 3337 (1955).

(7) A. Gandini and C. Costanza, *Gazz. chim. ital.*, **67**, 104 (1937); *C. A.*, **31**, 6614^4 (1937).

(8) (a) E. Shaw, THIS JOURNAL, **71**, 67 (1949); (b) K. G. Cunningham, G. T. Newbold, F. S. Spring and J. Stark, *J. Chem. Soc.*, 2091 (1949).

(9) R. Adams and S. Miyano, THIS JOURNAL, **76**, 3168 (1954).

(10) A. Lott and E. Shaw, *ibid.*, **71**, 70 (1949).

tion of several compounds. The principal product has been identified as 5-benzoyloxy-2-pyridone (V). This product V is a neutral compound hydrolyzed by dilute alkali to benzoic acid. Two equivalents of alkali are consumed in the alkaline hydrolysis consistent with the assigned structure. The ultraviolet absorption characteristics present a very clear-cut summation of the absorption characteristics of benzoic acid and 2-pyridone. The maxima occur at 233 mμ (log ϵ 4.18); 276 mμ (log ϵ 3.58); 284 mμ (log ϵ 3.58); and 306 mμ (log ϵ 3.62). Those of 2-pyridone occur at 229 mμ (log ϵ 3.85) and 300 mμ and those of benzoic acid at 228 mμ (log ϵ 4.05); 273 mμ (log ϵ 2.94); and 280 mμ (log ϵ 2.85). The infrared spectra shows absorption bands at 5.79 μ characteristic of the carbonyl stretching band in benzoates[11] and bands at 7.87 and 8.79 μ characteristic of carbon-oxygen stretching frequencies in benzoates. These data establish without doubt the assigned benzoate structure V. Furthermore, this establishes that the 2-pyridone portion of the ketone is a more effective electron donor than the phenyl group since it has previously been established[12] in such oxidations that the portion of the ketone most able to accept a positive charge becomes the alcoholic, or phenolic, portion of the ester.

Acknowledgment.—The authors wish to acknowledge with appreciation a grant from the Smith, Kline and French Company in support of this research and grants from the Research Corporation and Brown–Forman Industries for the purchase of the infrared spectrophotometer used in these studies.

Experimental[13,14]

The coumalyl chloride used in the following experiments was obtained by the method previously described[1] as a white, crystalline material, b.p. 113–117° (3 mm.); m.p. 76°. *p*-Methoxybenzoyl-2-pyrone, m.p. 153–154.5°, was prepared as previously described.[1]

The details for the preparation of 5-benzoyl-2-pyrone will be given. The other 5-aroyl-2-pyrones listed in Table I were prepared similarly. The crude *p*-ethyl derivative was extracted from an insoluble brown solid by-product by extraction in a Soxhlet with petroleum ether prior to recrystallization. Yields and analytical data are given in Table I for each compound.

5-Benzoyl-2-pyrone (I, R = H).—Fifteen and eight-tenths grams (0.10 mole) of freshly prepared coumalyl chloride dissolved in 40 ml. of benzene was added dropwise (30 minutes) to 41.2 g. (0.31 mole) of aluminum chloride in 60 ml. of benzene. After the addition was complete the dropping funnel was replaced with a thermometer and the mixture raised to a temperature of 55° for four hours with continuous stirring. Heating and stirring were discontinued and the reaction mixture allowed to stand overnight. Slight warming was necessary to obtain a liquid mixture which was poured over 100 g. of ice and 10 ml. of concentrated hydrochloric acid. The reaction vessel was rinsed cautiously with cold, dilute hydrochloric acid (5%) and the rinsing liquid added to the ice mixture. A volume of petroleum ether (b.p. 30–60°) equal to that of the organic layer was added to the resulting mixture, and the precipitated product collected on a filter washed with 50 ml. water, two 50-ml. portions of 5% bicarbonate solution, and finally with 50 ml. water. Air drying produced 18.6 g. (93%) of crude 5-benzoyl-2-pyrone. Two recrystallizations from benzene-petroleum ether gave white flakes, melting at 114.5–115°.

Oxidation of 5-(*p*-Toluyl)-2-pyrone.—One gram of 5-(*p*-toluyl)-2-pyrone (0.0046 mole) was maintained at 60° for 16 hours in a solution of 5 ml. of 30% hydrogen peroxide and 5 ml. of glacial acetic acid. The solution was evaporated to approximately one-half of its volume and an equal volume of distilled water added. Small white crystals separated (0.30 g., 48%). These crystals gave a melting point of 179–182°. Mixed melting point with an authentic sample of *p*-toluic acid (m.p. 179.6°) gave no depression of melting point.

The pyridones, except the dimethylaminoethyl derivative described in detail below, were prepared by heating the pyrone with ammonia or an amine. Details for typical procedures will be given. Data on the reactions and characterization of the products are given in Tables II and III.

5-Benzoyl-2-pyridone (II, R = H).—A solution of 1.0 g. (0.005 mole) of 5-benzoyl-2-pyrone in 10 ml. of concentrated ammonium hydroxide was boiled gently. Twenty ml. of water was added in small increments as the excess ammonia was driven off. The finely divided solid product was collected on a filter, washed first with water, then with a few drops of cold methanol and finally air dried, to give 0.87 g. (88%) of tan microcrystalline material, m.p. 192–195°. Two recrystallizations from aqueous methanol gave short white needles, m.p. 196–197.5°. This compound was soluble in dilute sodium hydroxide and insoluble in dilute acid.

Oxidation of 5-(*p*-Chlorobenzoyl)-2-pyridone.—A suspension of 0.3 g. of 5-(*p*-chlorobenzoyl)-2-pyridone in 20 ml. of water was refluxed with 1.5 g. of potassium permanganate in 30 ml. of 5% sodium hydroxide. Acidification gave 0.09 g. of white microcrystalline material, m.p. 227–233°. One recrystallization from water gave fine white crystals, m.p. 238–240°. Reported m.p. of *p*-chlorobenzoic acid, 240–242°.[15]

N-(β-Phenylethyl)-5-benzoyl-2-pyridone (III, R = H, R′ = $C_6H_5CH_2CH_2$).—One gram (0.005 mole) of 5-benzoyl-2-pyrone was refluxed with 2 ml. of β-phenylethylamine in 30 ml. of 50% ethanol-water mixture for 20 minutes. Five ml. of concentrated ammonium hydroxide was added and the solution allowed to cool. The product precipitated as an oil which solidified to give 0.98 g. (65% of theory) of gray semicrystalline material, melting below 100°. Two recrystallizations of this material from ethanol-water mixture gave very light yellow crystals, m.p. 112.5–114°.

N-(Dimethylaminoethyl)-5-benzoyl-2-pyridone (III, R = H, R′ = $(CH_3)_2NCH_2CH_2$).—Three and six-tenths grams (0.025 mole) of dimethylaminoethyl chloride hydrochloride was dissolved in 60 ml. of dry methanol containing 4.2 g. (0.075 mole) of potassium hydroxide. An exothermic reaction occurred shortly and the mixture was warmed gently for ten minutes. After cooling of this mixture, the precipitated potassium chloride was filtered off and 5.0 g. (0.025 mole) of 5-benzoyl-2-pyridone were added. The mixture was refluxed for six hours, acidified with 6 *N* hydrochloric acid, and extracted with ether for 24 hours in a continuous extractor. This ether extract upon evaporation left 3.1 g. (62%) of impure 5-benzoyl-2-pyridone. The aqueous layer left in the extractor was made basic with potassium hydroxide and extracted again with fresh ether for 24 hours. This ether extract was dried and evaporated under reduced pressure to give 0.9 g. (13.3%) of impure crystals, m.p. 89–92°. Two recrystallizations of this material from aqueous ethanol gave flat, pale yellow needles, m.p. 106.5–107.5°.

N-Amino-5-benzoyl-2-pyridone (IV, R = H, R′ = H).—One gram (0.005 mole) of 5-benzoyl-2-pyrone in 10 ml. of hot 50% ethanol-water mixture was treated with 15 drops of aqueous hydrazine solution (64%), with shaking during the addition. Upon cooling, 0.75 g. (70%) of pink crystals of N-amino-5-benzoyl-2-pyridone separated. The crude material melted at 165–166.5°. Two recrystallizations from 30% aqueous alcohol gave pale pink diamonds, m.p. 166.5–167.5°. This compound was soluble only in concentrated hydrochloric acid.

Anal. Calcd. for $C_{12}H_{10}O_2N_2$: N, 13.08. Found: N, 13.24, 13.33.

One-tenth gram of N-amino-5-benzoyl-2-pyridone dissolved in 2 ml. of ethanol and 2 ml. of concentrated hydrochloric acid was cooled in an ice-bath during the addition of 0.3 g. of potassium nitrite in 2 ml. of water. A white crys-

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[11] R. N. Jones, P. Humphries and K. Dobriner, *ibid.*, **72**, 956 (1950).

[12] W. D. Emmons and G. B. Lucas, *ibid.*, **77**, 2287 (1955).

[13] Microanalyses by Micro Tech Laboratories, Skokie, Illinois.

[14] All melting points are corrected.

[15] J. J. Stubbs and C. E. Senseman, *Ind. Eng. Chem.*, **28**, 559 (1936).

TABLE II

5-AROYL-2-PYRIDONES

R of formula II	M.p., °C.	Yield,[a] %	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Absorption data Ultra-violet[b]	Infrared[c]					
H	196–197.5	88	72.35	72.33	4.55	4.54	251(3.83) 290(4.14)	3.0–4.0[b]	6.02s	6.14vs[f]	6.98s	7.92s	13.17s 14.01s
CH_3	197–198.5	86			6.57[d]	6.59[d]	263sh 292(4.30)	3.2–4.0[b]	6.02s	6.14vs	7.01s	7.97s	12.02s
C_2H_5	158–159	79	73.99	73.88	5.77	5.84	263sh 291(4.37)						
Br	204.5–205.5	86	51.82	52.44	2.90	3.03	265(4.16) 293(4.31)	3.2–4.0[b]	6.03s	6.15vs	7.01s	7.97s	11.98s
Cl	251–253	80			6.00[d] 15.18[e]	6.60[d] 15.21[e]	260(4.00) 293(4.19)	3.2–4.0[b]	6.01s	6.15vs	7.00s	7.94s	11.82s

[a] All were recrystallized from aqueous methanol. [b] See footnote *b*, Table I. [c] See footnote *c*, Table I. [d] Nitrogen. [e] Chlorine. [f] This band appeared at 6.08 μ in chloroform.

TABLE III

N-SUBSTITUTED-5-AROYL-2-PYRIDONES

R	Formula III R′	M.p., °C.	Yield,[a] %	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Ultraviolet absorption data[b]	
H	CH_3	181.5–182.5	60M	73.22	73.01	5.30	5.22	252(3.87)	290(4.18)
H	$C_6H_5CH_2$	133.5–135	35E	78.87	78.68	5.23	5.37	252(3.86)	290(4.16)
H	$C_6H_5CH_2CH_2$	112.5–114	65E	79.18	78.96	5.65	5.90	250(3.74)	294(4.04)
H	$3,4(CH_3O)_2C_6H_4CH_2CH_2$	154.5–156	73E	72.71	72.77	5.82	5.90	252(3.84) 235sh	289(4.11)
H	$-CH_2CH_2$[e]	197–198	71E			6.60	6.64[d]		
CH_3	CH_3	147–148	40E	73.99	73.88	5.77	5.84	263sh	290(4.23)
CH_3	$C_6H_5CH_2CH_2$	116–118	34E	79.47	79.23	6.03	6.21	261sh	294(4.18)
H	$(CH_3)_2NCH_2CH_2$	106.5–107.5	13E	71.09	70.90	6.71 10.35	6.73 10.22[d]	250(3.88)	293(4.16)
H	$(C_2H_5)_2NCH_2CH_2$	83.5–85.5	68[e]M			9.39	9.24[d]		
H	$\underbrace{CH_2CH_2OCH_2CH_2}NCH_2CH_2CH_2$	136–137	67[f]E			8.58	8.46[d]	251(3.88)	293(4.18)
Cl	$\underbrace{CH_2CH_2OCH_2CH_2}NCH_2CH_2CH_2$	102.5–103.5	61E			7.77	7.64[d]		
H	*p*-$H_2NC_6H_4$	232–233	55E			9.65	9.68[d]	248(4.11)	290(4.20

[a] Recrystallized from E, aqueous ethanol; M, aqueous methanol. [b] See footnote *b*, Table I. [c] Ethylene bis compound from ethylenediamine. [d] Nitrogen. [e] Hydrochloride, m.p. 120–121°. [f] Hydrochloride, m.p. 239–240°.

TABLE IV

ABSORPTION DATA FOR N-AMINO-5-AROYL-2-PYRIDONES AND RELATED COMPOUNDS

2-Pyridone	Ultraviolet[a]		Infrared[b]					
N-Amino-5-benzoyl	247(4.01)	295(4.26)	3.04m	6.00s	6.14s	6.50m 6.97s	7.82s	13.35s 13.96s
N-Anilino-5-benzoyl		288(4.33)	3–4[b]	5.92s	6.18s	6.88s	8.15vs	13.00s 14.28s
N-Anilino-5-toluyl	272(4.31)	290(4.25)	3–3.8	5.94s	6.18s	6.99s	8.06vs	13.14s 14.60s
N-Hydroxy-5-benzoyl	228(4.13)	290(4.22)	3.0–4.0[b]	5.98	6.15s	7.00s	7.80s	13.00s 14.50s
5-Benzoyloxy	233(4.18) 276(3.58)	284(3.58) 306(3.62)	......	5.79	6.12s	7.87s	8.79m	14.20s

[a] See footnote *b*, Table I. [b] See footnote *c*, Table I.

talline material (0.1 g.) melting at 195–197° was gathered on a filter. Mixed melting point with an authentic sample of 5-benzoyl-2-pyridone (m.p. 196–197.5°) gave no depression of melting point.

N-Anilino-5-benzoyl-2-pyrone (IV, R = H, R′ = C_6H_5).—One-half gram of 5-benzoyl-2-pyrone (0.0025 mole) was dissolved in 10 ml. of ethanol made acidic with one drop of dilute hydrochloric acid. Phenylhydrazine (0.5 ml.) was added and the mixture refluxed for a few minutes. Upon slow cooling 0.22 g. (30%) of fine tan crystals formed, m.p. 230°. Two recrystallizations from ethanol–water mixture gave light tan needles, melting at 230–231°. This compound was stable to dilute base and was insoluble in both dilute acid and dilute base.

Anal. Calcd. for $C_{18}H_{14}O_2N_2$: C, 74.47; H, 4.86. Found: C, 74.38, 74.30; H, 4.90, 4.90.

N-Anilino-5-toluyl-2-pyrone (IV, R = CH_3, R′ = C_6H_5).—One-half gram of 5-(*p*-toluyl)-2-pyrone (0.0023 mole) in 10 ml. ethanol, one drop of hydrochloric acid and 0.5 ml. phenylhydrazine were refluxed briefly. On standing 0.22 g. (31%) of long white needles formed in clusters. Two recrystallizations from methanol–water gave white needles melting at 178–179°. This compound was insoluble in both dilute acid and dilute base.

Anal. Calcd. for $C_{19}H_{16}O_2N_2$: N, 9.27. Found: N, 9.36, 9.24.

N-Hydroxy-5-benzoyl-2-pyrone (III, R = H, R′ = OH).—One gram (0.005 mole) of 5-benzoyl-2-pyrone was refluxed for a few minutes with 1.0 g. of hydroxylamine hydrochloride (0.015 mole) in a solution of 5 ml. of pyridine and 5 ml. of ethanol. The mixture was filtered hot and 6 *N* hydrochloric acid was added dropwise until a thick flocculent precipitate was obtained. The mixture was allowed to cool and filtered to give a tan powder. Recrystallization from 70% aqueous ethanol gave 0.63 g. (59%) of tan, plate-like crystals. Two recrystallizations from ethanol–water gave white plates, melting at 198–199°. This compound was soluble in cold bicarbonate solution, and in dilute base. It could be titrated as an acid with sodium hydroxide. Oxidation with alkaline permanganate gives benzoic acid. Potentiometric titration gave a pK_a value of 5.13.

Anal. Calcd. for $C_{12}H_9O_3N$: C, 66.97; H, 4.22; N, 6.51; neut. equiv., 215.2. Found: C, 67.05, 67.13; H, 4.17, 4.32; N, 6.64, 6.51; neut. equiv., 217.

5-Benzoyloxy-2-pyridone (V).—One gram of 5-benzoyl-2-pyridone was dissolved in 6 ml. of 37% hydrogen peroxide solution and 6 ml. of glacial acetic acid. The pyridone went into solution as the mixture was heated to and maintained at 55° for 12 hours. Water was added to the warm solution until a very slight cloudiness was noted. Fine tan needles separated and were filtered, washed with water several times and air dried to give 0.34 g. (31%) of 5-benzoyloxy-2-pyridone. This material gave a weak greenish-brown color with acidic ferric chloride. Upon addition of enough dilute sodium hydroxide to this test solution to make it basic, and then reacidifying with hydrochloric acid, a darker red-brown ferric chloride test was obtained.

Two recrystallizations of this material from alcohol-water mixture gave fine light tan needles, m.p. 187–188°. This compound was soluble in base, with the appearance of a mossy green color, insoluble in acid and water.

Anal. Calcd. for $C_{12}H_9O_3N$: C, 66.97; H, 4.22; N, 6.51; sapon. equiv., 107.5. Found: C, 67.31, 67.35; H, 4.12, 4.25; N, 6.43, 6.46; sapon. equiv., 109.

5-Benzoyl-2-pyridone Sodium.—One gram (0.005 mole) of 5-benzoyl-2-pyridone was stirred with 7 ml. of hot 10% sodium hydroxide. The pyridone dissolved and fine white needles reappeared immediately and upon cooling. These were filtered, washed with acetone and air dried giving 0.85 g. (71%). One recrystallization from large volumes of dry acetone gave short white needles, m.p. 261–262°. A sample of this material melted and resolidified when introduced into the melting point bath at temperatures above 140°. Upon slowly raising the melting point bath containing the salt, this change took place too gradually to be visible.

Both the crystalline material first obtained and a sample fused at 150° for an hour yielded the original pyridone on acidification of an aqueous solution. The compound gave a strong alkaline test with moist red litmus paper and burned to leave an alkaline ash. The analysis of the crystalline material first obtained indicated two molecules of water of crystallization.

Anal. Calcd. for $C_{12}H_8O_2NNa \cdot 2H_2O$: C, 56.04; H, 4.70. Found: C, 56.43, 56.37; H, 4.97, 5.19.

3-Bromo-5-benzoyl-2-pyridone.—One gram (0.005 mole) of 5-benzoyl-2-pyridone dissolved in 15 ml. of hot methanol was treated with liquid bromine until a permanent color of bromine remained. After about a minute a heavy crop of short white needles separated, were filtered, washed with water and methanol and air dried to give 1.1 g. (79%) of product melting at 248–255°. Two recrystallizations from large volumes of ethyl acetate gave short white needles, m.p. 255–257°. This compound was insoluble in water and only slightly soluble in all organic solvents tested, but dissolved readily in dilute sodium hydroxide.

Anal. Calcd. for $C_{12}H_8O_2NBr$: Br, 28.73. Found: Br, 28.72.

N-Methyl-3-bromo-5-benzoyl-2-pyridone.—One and two-tenths grams (0.0056 mole) of N-methyl-5-benzoyl-2-pyridone dissolved in 20 ml. of hot ethanol was treated with liquid bromine until the color of bromine persisted briefly. One and three-tenths grams (78%) of white crystals separated after a few minutes. Two recrystallizations from large volumes of ethanol gave white prisms melting at 201–202°. This material was insoluble in water and dilute sodium hydroxide, and only slightly soluble in the common organic solvents.

Anal. Calcd. for $C_{12}H_{10}O_2NBr$: Br, 27.36. Found: Br, 27.36.

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2-Pyrones. XIX. 3-Hydroxy-2-pyrone[1] and 4-Arylhydrazono-2,3-pyranones

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3-Hydroxy-2-pyrone (isopyromucic acid) has been prepared by the potassium bisulfate dehydration of mucic acid and purified by a new technique as a colorless solid giving a blue ferric chloride test. Comparisons of its infrared absorption data with those of 3-methoxy-2-pyrone confirm the presence of a hydrogen-bonded hydroxyl group as in the structures IIa, IIb and IIc. Coupling with diazonium salts gives unstable, deeply colored products for which the infrared absorption characteristics are in accord with the 4-arylhydrazono-2,3-pyronone structure VI.

Although the acid-catalyzed transformation of mucic acid to pyromucic acid (furan-2-carboxylic acid) and dehydromucic acid (furan-2,5-dicarboxylic acid) has received continued attention since the reaction was originally observed by Scheele in the late eighteenth century,[2] the competitive conversion of mucic acid to 3-hydroxy-2-pyrone, originally reported by Limpricht,[3] who named the product isopyromucic acid, has received scanty attention. As a result little is known of the chemistry of this interesting structure and no reliable directions for its preparation are available. In this paper we wish to report the results of our studies on the preparation, isolation and characterization of this compound, our studies on its reactions with aryldiazonium compounds and our analysis of its structure in terms of comparisons of its infrared absorption spectrum with that of 3-methoxy-2-pyrone.

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(1) The systematic *Chemical Abstracts* name for this structure (formulas I and IIa,b,c) can be 3-hydroxy-2-oxo-2H-pyran; 2H-pyran-2,3(4H)-dione; 2H-pyran-2-one, 3-hydroxy; or 5-hydroxy-2-oxo-4-pentenoic γ-lactone. It has also been known as isopyromucic acid. *Chemical Abstracts* indexing policy is not decisive for these structures and although there has been an announced policy to index these compounds as lactones, many have been indexed as hydroxypyranones or pyrandiones depending upon whether the keto or enol form is used as a basis for indexing. The pyrone nomenclature is used in this paper because of its relation to other compounds we are studying which also contain this structural unit.

Selection of suitable nomenclature for the arylhydrazones (formula VI) poses similar problems. Consistent with the pyranone nomenclature these are 4-arylhydrazones which may properly be named 4-arylhydrazono-2,3-dioxo-3,4-dihydro-2H-pyrans or 4-arylhydrazono-2,3-dioxo-2,3-dihydro-4H-pyrans. The pyronone name represents a convenient extension of the pyranone–pyrone nomenclature which has previously been used for similar structures derived from dehydroacetic acid types. Systematically, replacement of "an" in a name by "on" implies replacement of $-CH_2-$ by $-CO-$ and in this sense pyranone is a contraction of a dihydropyranone, not of a pyranone structure Again *Chemical Abstracts* will probably index these structures as γ-lactones of 3-arylhydrazono-5-hydroxy-2-keto-4-pentenoic acid.

(2) A. P. Dunlop and F. N. Peters, "The Furans," Reinhold Publ. Co., New York, N. Y., 1953, pp. 486–487, 572–573.

(3) H. Limpricht, *Ann.*, **165**, 257 (1873).