Anal. Calcd. for $C_{24}H_{28}N_2O$: N, 7.77. Found: N, 8.05.

When two equivalents of *p*-dimethylaminobenzaldehyde and one equivalent of cyclohexanone were refluxed in a solution of 0.3% sodium hydroxide in 50% ethanol, the yield of 2,6-bis-(*p*-dimethylaminobenzylidene)-cyclohexanone was only 12.5%. A considerable amount of lower melting point material, 66–68°, was recovered from the reaction mixture by diluting the filtrate with water.

2,6-Bis-(*p*-dimethylaminobenzyl)-cyclohexanone.—One gram of 2,6-bis-(*p*-dimethylaminobenzylidene)-cyclohexanone was dissolved in a mixture of 150 ml. of ethanol, 6 ml. of concentrated hydrochloric acid and 15 ml. of water. Two hundred milligrams of 10% palladium-on-carbon (J. T. Baker) was added and the hydrogenation carried out at 20 lb. pressure at room temperature. The calculated amount of hydrogen was taken up within 15 minutes. The catalyst was filtered off and the colorless solution was neutralized with 10% sodium carbonate and diluted with an equal volume of water. The resulting colorless precipitate was filtered with suction, washed with water and recrystallized from 95% ethanol, m.p. 136–137°.

Anal. Calcd. for $C_{24}H_{32}N_2O$: N, 7.69; C, 79.08; H, 8.85. Found: N, 7.92; C, 79.30; H, 9.03.

2-(*p*-Acetoxyphenyl)-nitrocyclohexane.—To a solution of 1 g. (0.00383 mole) of 4-nitro-5-(*p*-acetoxyphenyl)-cyclohexene in 200 ml. of absolute ethanol was added 0.1 g. of 10% palladium-on-carbon (J. T. Baker) and hydrogenation was carried out at 30 lb. pressure at room temperature. About a one-to-one molar ratio of hydrogen was taken up within 15 minutes and the uptake of hydrogen then came to a stop. The catalyst was filtered off and the ethanol removed *in vacuo*. The crude product was recrystallized from 95% ethanol, giving a colorless material, m.p. 92–93°. The product is not soluble in 10% hydrochloric acid, indicating that the nitro group was not reduced.

Anal. Calcd. for $C_{14}H_{17}NO_4$: N, 5.32; C, 63.86; H, 6.51. Found: N, 5.36; C, 64.11; H, 6.46.

Analyses.—Analyses are by the Microanalytical Division of the Department of Chemistry, University of California.

Melting points.—All melting points are corrected.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Spectra as a Guide to Structure in the Hydroxypyrone and Hydroxypyridone Series

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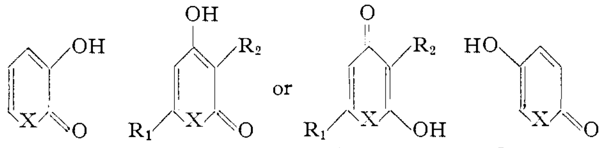
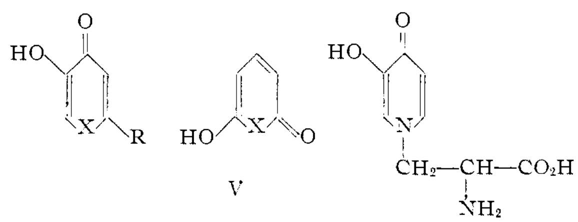
The ultraviolet spectra of 4-hydroxy-2-pyrones and pyridones (or their enol tautomers) are shifted hypsochromically in alkaline solution, while those of 3-hydroxy-4-pyrones or pyridones and of 2-hydroxy-3-pyridones are shifted bathochromically.

In the course of a recent structural investigation,[1] certain degradation products were shown to be N-alkylated hydroxypyridones, although no basis existed for a choice of a detailed expression from among the alternative types I–V(X = N).[2] Since the confirmation of structure by independent synthesis of even simple members of these classes of substances is often tedious and difficult,[3] a simple diagnostic procedure was desirable. Although the work we report here does not deal with all of the structures I–V, it provides a simple method for distinguishing pyridones (X = N) or pyrones (X = O) of the type II from those of types I and IV.



I, X = NCH_3 IIa, $R_1 = CH_3$; R_2 = H; X = O III
b, $R_1 = CH_3$; $R_2 = C_2H_5$; X = O
c, $R_1 = CH_3$; $R_2 = COCH_3$; X = O
d, $R_1 = CH_3$; $R_2 = C_2H_5$; X = NCH_3
e, $R_1 = CH_3$; R_2 = H; X = NCH_3



V

IVa, R = CH_2OH; X = O VI
b, R = H; X = NCH_3
c, R = CH_2OH; X = NCH_3

We were led to investigate a spectroscopic approach for two reasons: (i) the expectation that any distinguishing criteria found in the ultraviolet behavior of pyrones would apply to pyridones[4]; and (ii) the unusual *hypsochromic* shift of the ultraviolet absorption maximum in alkaline solution observed[5] with pyrones of the type II (*e.g.*, triacetic lactone, IIa). Accordingly, we measured the ultraviolet absorption spectra in neutral and basic methanol or ethanol of I, IIa-d and IVa-c. All of these substances except IVc and IId were known.[6] We have prepared IVc from methylamine and kojic acid (IVa), and IId from methylamine and desoxodehydroacetic acid (IIb). Table I shows the data.

Conclusions.—(i) The general similarities between the spectra of pyrones and the corresponding pyridones apply to this series as well as to the simpler mother substances previously examined.[4] However, certain other regularities of behavior observed with the simple models[4] are not obeyed here. In particular, it was previously observed[4] that the integrated absorption intensity could be correlated with the square of the distance between the hetero

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[1] J. A. Berson and W. M. Jones, THIS JOURNAL, **78**, in press (1956).

[2] A classical example of the same kind of problem developed during the determination of the structure of the alkaloid leucenol (leucaenine), VI.[3]

[3] (a) R. Adams, S. J. Cristol, A. A. Anderson and A. A. Albert, THIS JOURNAL, **67**, 89 (1945); (b) A. F. Bickel and J. P. Wibaut, *Rec. trav. chim.*, **65**, 65 (1946); (c) J. P. Wibaut, *Helv. Chim. Acta*, **29**, 1669 (1946); (d) J. P. Wibaut and R. J. C. Kleipool, *Rec. trav. chim.*, **66**, 24, 459 (1947); (e) A. F. Bickel, THIS JOURNAL, **69**, 1801, 1805 (1947); (f) R. Adams and T. R. Govindachari, *ibid.*, **69**, 1806 (1947); (g) R. Adams, V. V. Jones and J. L. Johnson, *ibid.*, **69**, 1810 (1947); (h) R. Adams and V. V. Jones, *ibid.*, **69**, 1803 (1947).

[4] J. A. Berson, *ibid.*, **75**, 3521 (1953).

[5] J. A. Berson, *ibid.*, **74**, 5172 (1952).

[6] We are greatly indebted to Professor J. P. Wibaut (Amsterdam) for samples of I and IVb, and to Dr. W. M. McLamore (Charles Pfizer and Company) for a sample of kojic acid (IVa).

TABLE I

	Medium	λmax (mμ)[a]	log ε
Pyrones			
IIa	95% EtOH	283	3.78
IIa[b]	EtOH–NaOH[c]	278	3.84
IIb	95% EtOH	290	3.92
IIb[b]	EtOH–NaOH[c]	289	3.98
IIc[b]	95% EtOH	310	4.05
IIc[b]	EtOH–NaOH	294	3.91
IVa	MeOH	269	3.90
IVa	MeOH–KOH[d]	316	3.75
Pyridones			
IId	MeOH	287	3.87
IId	MeOH–KOH[e]	279	3.86
IIe[f]	H_2O or MeOH	282	3.81
I	MeOH	299	3.85
I	MeOH–KOH[e]	310	3.85
IVb	MeOH	281[g]	4.09
IVb	MeOH–KOH[d]	309	3.99
IVc	MeOH	284	4.14
IVc	MeOH–KOH[d]	313	4.00

[a] Only the intense long wave length maximum is reported. [b] Reference 5. [c] In a 2×10^{-4} *M* solution of sodium hydroxide in 95% ethanol. [d] In a 2.5×10^{-2} *M* solution of potassium hydroxide in methanol. [e] In a 2×10^{-3} *M* solution of potassium hydroxide in methanol. [f] Reported by H. M. Woodburn and M. Hellmann, *Rec. trav. chim.*, **70**, 813 (1951); spectrum in alkali not reported. [g] Reported (reference 3d) λ_{max} 278 mμ, log ε 4.31 (in water).

atom and the carbonyl oxygen. This rule fails with the hydroxypyridones. For example, the ratio of the squares of these distances for IVb *vs.* I is 0.35, whereas the ratio of the integrated intensities is 0.63.

(ii) Whereas the 3-hydroxy-4-pyridones and pyrones (type IV) and the 3-hydroxy-2-pyridone (I) show pronounced bathochromic shifts of the principal maximum in alkaline solution, the pyridones and pyrones of type II all show hypsochromic shifts. Although the direction of enolization of pyrones and pyridones of type II is not always certain,[7] this ambiguity does not detract from the usefulness of the results. Thus, a given unknown pyridone (or pyrone) may be enolized in a direction opposite to that of other members of the class. If its spectrum in neutral solution is different from that of known models, no use would be made of spectroscopic criteria of structure. If its spectrum in neutral solution is the same as that of known models, despite a different direction of enolization, the spectroscopic criterion is still valid, since either of a pair of enols of a given substance of type II would give the *same* enolate ion and, consequently, the hypsochromic shift would be observed.

We conclude that the ultraviolet absorption behavior in neutral and alkaline solution distinguishes hydroxypyrones and hydroxypyridones of type II from those of types I and IV.

Experimental[8]

1-Methyl-3-hydroxy-2-pyridone (I) was prepared in our laboratory by the method of Bickel and Wibaut.[3b] Our sample had m.p. 130–131° (capillary); reported[3b] m.p. 130–131°. It had substantially the same ultraviolet properties as an authentic sample supplied by Professor Wibaut. Incidentally, Professor Wibaut informs us that this material melts at 116–118° on a micro hot-stage.

1-Methyl-3-hydroxy-4-pyridone (IVb) was kindly supplied by Professor Wibaut, who informs us the m.p. is 224–227° (sealed capillary), 212–216° on the melting point microscope; reported[3d] m.p. 225–227° (capillary).

Kojic acid (IVa), supplied by Dr. W. M. McLamore, had m.p. 152–154°; reported[9] m.p. 152°.

1-Methyl-2-hydroxymethyl-5-hydroxy-4-pyridone (IVc).—A mixture of 5 g. of kojic acid and 50 cc. of 25% aqueous methylamine was heated on the steam-bath for 2.5 hours. The solution was cooled, stoppered and allowed to stand overnight. The water and excess methylamine were removed *in vacuo*, leaving a dark semi-solid mass. This material was recrystallized several times from ethanol (with Nuchar) to give 0.6 g. of small, colorless crystals, m.p. 225–227° dec., with darkening at 215° (capillary). The substance was soluble in water and acetic acid, sparingly soluble in alcohol. Its alcoholic solution gave a violet color with ferric chloride.

Anal. Calcd. for $C_7H_9O_3N$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.25; H, 6.07; N, 8.77.

1,6-Dimethyl-3-ethyl-4-hydroxy-2-pyridone (IId).—A solution of 0.513 g. of desoxodehydroacetic acid[5,10] (IIb) in 15 cc. of 25% aqueous methylamine was heated on the steam-bath for 4 hours. The water and methylamine were removed *in vacuo* at 70°, and the residue was recrystallized from 3 cc. of 95% ethanol to give 0.20 g. of IId as a colorless solid, m.p. 237–240° dec. Further recrystallization gave material of m.p. 238–240.5° dec. IId gave a bright red color with ferric chloride. It was soluble in sodium hydroxide, insoluble in bicarbonate, did not react with ethanolic picric acid. The Folin test was negative.

Anal. Calcd. for $C_9H_{13}O_2N$: C, 64.67; H, 7.84; N, 8.38. Found: C, 64.94; H, 7.88; N, 8.42.

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[7] (a) F. Arndt and S. Avan, *Ber.*, **84**, 343 (1951), have assigned the α-pyrone structure to triacetic lactone (IIa); (b) however, H. M. Woodburn and M. Hellmann, *Rec. trav. chim.*, **70**, 813 (1951), consider the direction of enolization in the corresponding pyridone (IIe) still uncertain.

[8] Melting points are corrected. The analyses are by Mr. W. J. Schenck. Ultraviolet spectra were taken with the Beckman spectrophotometer, model DU.

[9] T. Yabuta, *J. Chem. Soc. Japan*, **37**, 1185 (1916); *C. A.*, **17**, 1475 (1923).

[10] R. Malachowski and T. Wanczura, *Bull. intern. acad. polonaise*, **a**, 547 (1933); *C. A.*, **28**, 4421 (1934).