[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Mold Metabolites. IV. The Ultraviolet Absorption Spectra of Certain Aromatic Hydroxyketones

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In connection with another study[2] a number of alkyl substituted 2,4-dihydroxyacetophenones were prepared as models for the structures of certain pigments produced by molds. Because of the large number of naturally occurring compounds that contain the acylresorcinol type of nucleus, the syntheses of these compounds has been extended, and a study in a semisystematic manner of the effects of several variables on the ultraviolet absorption spectra of these substances has been undertaken.

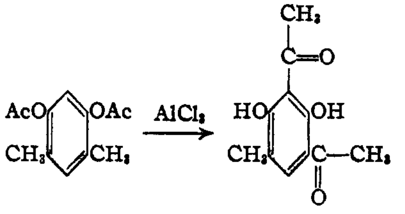
Two investigations have been made of the spectra of aromatic hydroxyaldehydes, ketones and their derivatives. Morton and Stubbs[3] reported the ultraviolet absorption[3] spectra of 2-, 3- and 4-hydroxyacetophenone, their respective methyl ethers and other related compounds. Lemon[4] investigated the spectra of several hydroxy- and methoxy-substituted aromatic aldehydes and ketones in neutral and basic media.

The present investigation is concerned with first, a correlation of the spectra of acetophenone, 2- and 4-hydroxyacetophenone, 2,4-dihydroxyacetophenone (I) and 2,6-dihydroxyacetophenone (II); second, with the effect on the spectra of methyl groups substituted first singly and then in pairs in all possible positions in the nucleus of I and II; and third, with the effect of solvent. The shifts of the spectral bands that accompany the variations in structure and environment of these molecules are very difficult to interpret, and the conclusions suggested by correlation of the following spectral data are only empirical.

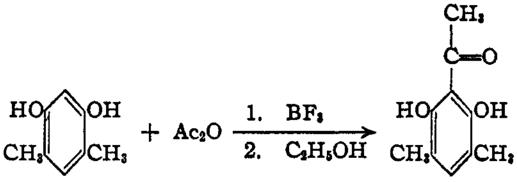
Compounds I, IV, V, VI, VII and VIII[5] were all prepared in connection with another study,[6] and references to the preparation of II, III, IX and X[5] are found in the experimental part.

Acetylation of 4,5-dimethylresorcinol[7] with acetyl chloride with aluminum chloride as catalyst produced XI.[5]

The preparation of XII proved to be quite difficult. Ordinary Friedel–Crafts reactions when applied to 4,6-dimethylresorcinol (XIII) did not give the desired product, and when a Fries rearrangement was run on the diacetate of XIII, one of the methyl groups was displaced to give XIV. Acylation of XIII was finally accomplished through the use of acetic anhydride with boron trifluoride etherate as catalyst. The methyl ethers were prepared from the parent phenols in the usual ways.



XIV



XIII XII

The ultraviolet absorption spectra were taken in a quartz Beckman spectrophotometer in three solvents, 50% ethanol–50% 0.10 N HCl solution, 0.01 N NaOH solution, and cyclohexane. Since practically all of the substances studied are phenols, the spectra of the compounds in basic solution are those of a mono anion, the alkali concentration being such that the second proton was not removed from the molecule. Thus the spectra of I and II in basic solution were not sensitive to *p*H changes of the solvent from 11 to 12.5, but at higher *p*H's the spectra were modified due to the removal of the second proton from the molecule. The anions in question undoubtedly are formed by the removal of a proton from the 4-hydroxyl group of 2,4-dihydroxyacetophenone and similar compounds, and from the 6-hydroxyl group of 2,6-dihydroxyacetophenone and similar compounds.

The Spectra of I and II

Table I summarizes the spectra data with which this study is concerned. The data indicate that the primary band of the acetophenone spectrum is shifted to the red by the introduction of *p*-substituents, the amount of shift correlating with the ability of that substituent to release electrons.[8] The introduction of an *o*-

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[2] Mold Metabolites, II and III, THIS JOURNAL, **70**, 4240 (1948).

[3] Morton and Stubbs, *J. Chem. Soc.*, 1347 (1940).

[4] H. W. Lemon, THIS JOURNAL, **69**, 2998 (1947).

[5] The identification of number with compound can be made by consulting Table I.

[6] Cram, THIS JOURNAL, **70**, 4240 (1948).

[7] Yanagita, *Ber.*, **71B**, 2269–2273 (1938).

[8] Doub and Vandenbelt, THIS JOURNAL, **69**, 2714 (1947), in their elegant correlation of the ultraviolet absorption spectra of mono and *p*-disubstituted benzene derivatives pointed out this trend. These authors referred to the first primary band ($\epsilon_M = 6 \times 10^3$ or more) as the absorption due to the displacement of the high intensity band of benzene ($\lambda \cong 200$ mμ) by the electronic effects of substituents on the benzene ring. The secondary band, which occurs at longer wave lengths, is easily differentiated from the first by its lower intensity.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRAL DATA

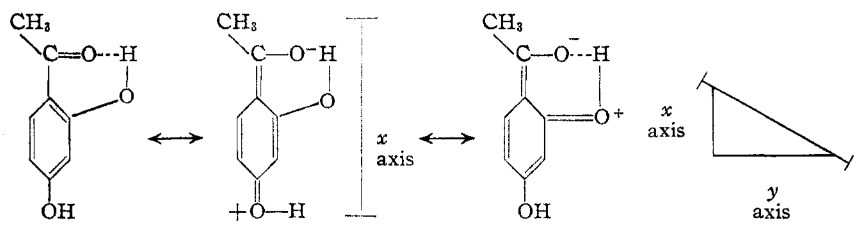
Acetophenone derivative	No.	Bands in acid sol.[a] 1st. prim. $\lambda_{max.}$[c]	log ε	Secondary $\lambda_{max.}$	log ε	Bands in basic sol.[b] 1st. prim. $\lambda_{max.}$	log ε	Secondary $\lambda_{max.}$	log ε	Bands in cyclohexane 1st. prim. $\lambda_{max.}$	log ε	Secondary $\lambda_{max.}$	log ε
Parent compound		246[d]	3.99	...	..	...	..	...	..	273[f]	4.11		
4-Methyl[d]		256	4.16	...	..	...	..	...	..	..	..	...	..
4-Hydroxy[d]		275	4.16	...	..	325	4.36	...	..	..	..	...	...
4-Methoxy[d]		277	4.19	...	..	...	..	...	..	..	..	...	..
2-Hydroxy[e]		252	3.97	327	3.50	257	3.76	359	3.71	256	4.02	329	3.63
2-Methoxy[e]		246	4.06	305	3.58	...	..	...	..	243	3.90	300	3.58
2,4-Dihydroxy	I	277	4.14	314	3.85	333	4.42	...	..	270	4.14	314	3.76
2,4-Dihydroxy-3-methyl	III	286	4.19	~[g]	..	332	4.43	...	..	276	4.06	318	3.57
2,4-Dihydroxy-5-methyl	IV	280	4.00	326	3.84	337	4.38	...	..	272	4.00	326	3.65
2,4-Dihydroxy-6-methyl	V	283	4.00	~[g]	..	330	4.07	...	..	275	4.01	321	3.62
2,4-Dihydroxy-3,5-dimethyl	VI	285	4.17	329	3.72	342	4.42	...	..	277	4.16	328	3.70
2,4-Dihydroxy-3,6-dimethyl	VII	291	4.01	~[g]	..	333	4.24	...	..	281	4.02	326	3.42
2,4-Dihydroxy-5,6-dimethyl	VIII	285	3.75	~[g]	..	348	3.93	...	..	277	4.00	332	3.70
2,6-Dihydroxy	II	270	4.05	345	3.45	284	3.88	381	3.59	263	3.92	334	3.36
2-Hydroxy-6-methoxy		274	4.04	340	3.46	282	3.46	334	3.32	270	4.05	335	3.54
2,6-Dimethoxy		267	3.49	~[g]	..	...	..	...	..	240	3.34	279	3.22
2,6-Dihydroxy-4-methyl	X	276	4.18	343	3.44	288	4.04	378	3.59	267	4.16	332	3.39
2,6-Dihydroxy-3-methyl	IX	273	4.09	357	3.47	285	3.94	394	3.58	266	4.05	344	3.48
2,6-Dimethoxy-3-methyl		283	3.27	~[g]	..	282	3.26	~[g]	..	282	3.27	...	..
2,6-Dihydroxy-3,4-dimethyl	XI	271	4.13	357	3.67	287	3.99	394	3.63	272	4.01	356	3.70
2,6-Dihydroxy-3,5-dimethyl	XII	275	4.05	363	3.46	288	3.88	407	3.39	268	4.05	353	3.06

[a] Solvent is 50% ethanol–50% 0.10 *N* HCl solution. [b] Solvent is 0.01 *N* NaOH solution. [c] Wave length given in mμ. [d] Doub and Vandenbelt (ref. 8). [e] Morton and Stubbs (ref. 3). [f] O'Shaughnessy and Rodebush, THIS JOURNAL, **62**, 2906 (1940); the spectrum was taken by these authors in *n*-hexane. [g] ~ stands for point of inflection.

substituent results in only a slight shift of the primary band[8] and at the same time in the emergence of a secondary band.[8] However, upon substitution of a second *o*-substituent both bands are equally affected.

The removal of a proton from the *p*-hydroxyl by solution in alkali produces an enormous shift of the primary band to approximately the position of the secondary, if originally present, as in the case of 2,4-dihydroxyacetophenone. The additive effect of the two bands in the same region is borne out by the increased intensity of the new band. Similar ionization of the *o*-hydroxyl is manifested by a shift of both bands, the greater effect being on the secondary.

The result of chelation in shifting the secondary band toward the red is also borne out by the data. Thus, methylation of all *o*-hydroxyl groups produced a marked shift toward the ultraviolet.



The above facts can be correlated if the various acetophenone derivatives are considered to absorb light along two non-identical optical axes, *x* and *y*, which are perpendicular to each other.[9] The longer optical axis (*x*) corresponds to electronic transitions associated with *p*-resonance contributions to the hybrid of the ground and excited states, and would seem to roughly correlate with the absorption of the primary band, whereas the shorter optical axis (*y*) is particularly sensitive to transitions associated with *o*-resonance forms, and correlates with the absorption of the secondary band. However, the vector defined by electronic oscillations between two functional groups substituted *ortho* to each other can be resolved into two components, one along each axis, and hence the primary band is also somewhat affected by *o*-substituents, particularly when *p*-substituents are missing. Thus an *o*-hydroxyl group shifts the primary band to the red less than a *p*-hydroxyl group, and unlike the latter produces a new secondary band. When a hydroxyl group is substituted in the 2-position of 4-hydroxyacetophenone, again a secondary band appears, and the primary band is shifted only slightly. Introduction of a second *o*-hydroxyl group shifts both bands toward the red. Also shifts to longer wave length that accompany the removal of a proton from the various phenols, as well as the relative sensitivity of the secondary band to chelation are interpretable in terms of the above treatment.

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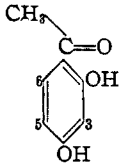
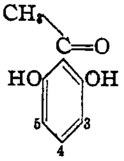
[9] This concept has been applied to the spectra of triphenylmethane dyes and other compounds by Lewis, Branch, Calvin and others; a discussion of the treatment is found in *Chem. Revs.*, **25**, 273 (1939), and **43**, 429 (1948).

TABLE II

EFFECT OF NUCLEAR SUBSTITUTION OF METHYL GROUPS ON THE SPECTRUM OF I AND II



I



II

		$\Delta\lambda^a$ for first primary band (mμ)				$\Delta\lambda^a$ for secondary band (mμ)			
Comp.	No.	Cyclohex. Found	Cyclohex. Calcd.	Acid Found	Base Found	Cyclohex. Found	Cyclohex. Calcd.	Acid Found	Base Found
3-Methyl I	III	+ 6	..	+ 9	− 1	+ 4	..	+12	..
5-Methyl I	IV	+ 2	..	+ 3	+ 4	+12	..	..	..
6-Methyl I	V	+ 5	..	+ 6	− 3	+ 7	..	..	..
3,5-Dimethyl I	VI	+ 7	+ 8	+ 8	+ 9	+14	+16	..	..
3,6-Dimethyl I	VII	+11	+11	+14	0	+12	+11	+15	..
5,6-Dimethyl I	VIII	+ 7	+ 7	+ 8	+15	+18	+19	..	..
3-Methyl II	IX	+ 3	..	+ 6	+ 1	+10	..	+12	+13
4-Methyl II	X	+ 4	..	+ 3	+ 4	− 2	..	− 2	− 3
3,4-Dimethyl II	XI	+ 9	+ 7	+ 1	+ 3	+22	+ 8	+12	+13
3,5-Dimethyl II	XII	+ 5	+ 6	+ 5	+ 4	+19	+20	+18	+26

[a] $\Delta\lambda = \lambda_{max.}$ of substituted compound minus $\lambda_{max.}$ of parent compound.

Effect on Spectra of the Nuclear Substitution of Methyl Groups in I and II

Table II records the displacements of each band of compounds I and II which result when methyl groups are substituted in all possible positions in the ring, first one at a time, and second in pairs. In cyclohexane where solvent–solute hydrogen bonding is eliminated, the substitution of methyl groups in pairs produces displacements which in all but one case are of almost the same value as the sum of the displacements due to methyl groups substituted singly in the same positions in the ring. This additive relationship holds for each band in each compound, the only exception being that of the displacement of the secondary band of 2,6-dihydroxy-3,4-dimethylacetophenone (XI) where the secondary band is found 14 mμ further toward the red than would be expected were the effect of the methyl groups only additive.

The additive relationship of the displacements of the bands can hold in acid and basic solution only if the effect of solvent-solute hydrogen bonding is constant from structure to structure. The data would indicate that this is roughly the case for the first primary bands of compounds related to I in acidic solution and for compounds related to II in basic solution and for the secondary bands of compounds related to II in acidic and basic solutions. Otherwise the data tend to vary in an erratic fashion suggesting variation of solvent–solute hydrogen bonding with the positions and number of methyl groups substituted in the ring.

The displacements of the two bands in acid solution due to the substitution of methyl groups in I and II show little correlation with the displacements of the same bands of the same compounds in basic solution, the only exception being the shifts of the secondary bands of the derivatives of II. Here the $\Delta\lambda$'s in acid and base are equal for each compound except in the case of 2,6-dihydroxy-3,5-dimethylacetophenone (XII). This anomaly can be explained in the following way. Since the 3- and 5-positions are equivalent, $\Delta\lambda$ for XII should be twice that of 2,6-dihydroxy-3-methylacetophenone, and such is the case when the molecule is in anionic form, but not when in the phenolic form. Molecular models of XII indicate that complete coplanarity of the hydroxyl group in the 6-position with the ring system is opposed by the methyl group attached to the ring in the 5-position on one side and by the methyl group of the ketone group on the other (the ketone group and the ring are assumed to be coplanar due to resonance and chelation effects). Since full resonance of the hydroxyl group with the ring involves some double bond character to the oxygen–carbon bond, such resonance is inhibited by the inability of the two systems to assume a coplanar configuration, and the displacement due to the introduction of the second methyl group is less than it otherwise would be. In the anion of XII, however, since the proton has been removed, steric inhibition of resonance is no longer present and the expected displacement is observed.

The substitution of methyl groups in each of the open positions of I should affect the absorption of light along both the x and y axes as is found to be the case. Substitution of a methyl group in the 4-position of II should have little effect on the y axis, and only a negligible value of $\Delta\lambda$ was observed.

Effect of Solvent–Solute Hydrogen Bonding on the Spectra of I, II and Derivatives

The data in Table III indicate that the first primary bands of all the compounds listed except that of XI are displaced 7–10 mμ toward longer

TABLE III

DISPLACEMENTS OF BANDS DUE TO INTERMOLECULAR HYDROGEN BONDING

Acetophenone derivative	No.	Prim. band $\Delta\lambda^{a}_{A-C}$	Sec. band $\Delta\lambda^{a}_{A-C}$
2,4-Dihydroxy	I	+ 7	0
2,4-Dihydroxy-3-methyl	III	+10	..
2,4-Dihydroxy-5-methyl	IV	+ 8	0
2,4-Dihydroxy-6-methyl	V	+ 8	..
2,4-Dihydroxy-3,5-dimethyl	VI	+ 8	+ 1
2,4-Dihydroxy-3,6-dimethyl	VII	+10	..
2,4-Dihydroxy-5,6-dimethyl	VIII	+ 8	..
2,6-Dihydroxy	II	+ 7	+11
2,6-Dihydroxy-3-methyl	IX	+ 7	+13
2,6-Dihydroxy-4-methyl	X	+ 9	+11
2,6-Dihydroxy-3,4-dimethyl	XI	− 1	+ 1
2,6-Dihydroxy-3,5-dimethyl	XII	+ 7	+10

[a] $\Delta\lambda_{A-C} = \lambda_{max.}$ in acid solution minus $\lambda_{max.}$ in cyclohexane.

wave lengths in acid solution compared to cyclohexane. This effect is undoubtedly due to solvent–solute hydrogen bonding which is possible in hydroxylic but impossible in hydrocarbon solvent. The lack of solvent effect for XI is difficult to explain and recalls the anomalous position of the secondary band of this same compound in cyclohexane.

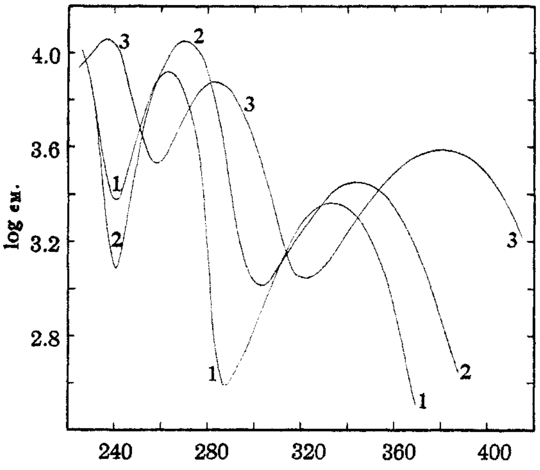


Fig. 1.—Ultraviolet absorption spectra of 2,6-dihydroxyacetophenone II: curve 1, in cyclohexane; curve 2, in 50% ethanol–50% 0.10 *N* HCl solution; curve 3, in 0.01 *N* NaOH solution.

The exact positions of the secondary bands of III, V, VII and VIII in acid solution are obscured by their proximity to the first primary band, but the positions of I, IV and VI indicate that the secondary band in these molecules has not been altered by solvent effects. The secondary bands of II, IX and X have each been displaced 10–13 mμ in going from cyclohexane to acid solution, again compound XI showing an anomalous behavior in not being sensitive to solvent effects.

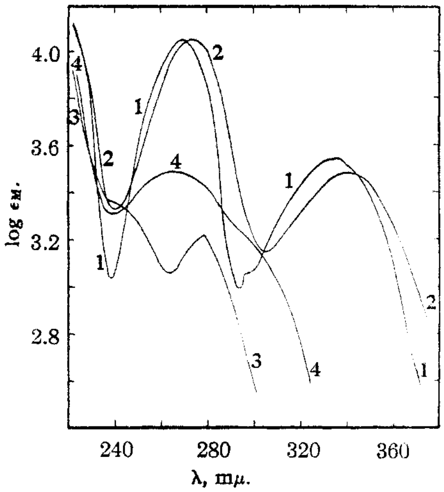


Fig. 2.—Ultraviolet absorption spectra of 2-hydroxy-6-methoxyacetophenone: curve 1, in cyclohexane; curve 2, in 50% ethanol–50% 0.10 *N* HCl solution. Ultraviolet absorption spectra of 2,6-dimethoxyacetophenone: curve 3, in cyclohexane; curve 4, in 50% ethanol–50% 0.10 *N* HCl solution.

Comparison of the spectra of 2,6-dimethoxyacetophenone (Fig. 3) with that of 2,6-dimethoxy-3-methylacetophenone (Fig. 4) indicates very large solvent effects in the former substance that are absent in the latter compounds. The spectra of these compounds are quite different from those of the free phenols, II and IX, the difference being at least partially attributable to the chelation present in the non-methylated compounds.

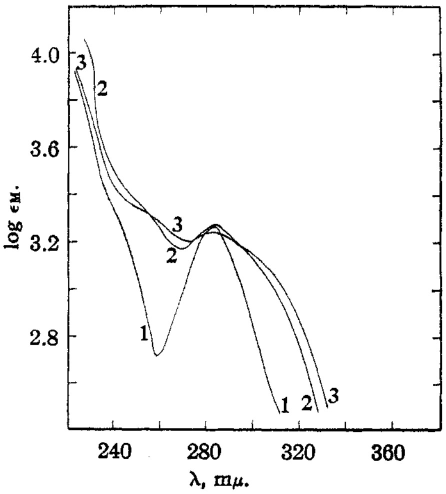


Fig. 3.—Ultraviolet absorption spectra of 2,6-dimethoxy-3-methylacetophenone: curve 1, in cyclohexane; curve 2, in 0.10 *N* HCl solution; curve 3, in 0.01 *N* NaOH solution.

Experimental

General.—Compound II was prepared according to the method of Baker,[10] m. p. 155–156° (lit.[10] 156–157°), III

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[10] Baker, *J. Chem. Soc.*, 1953 (1934).

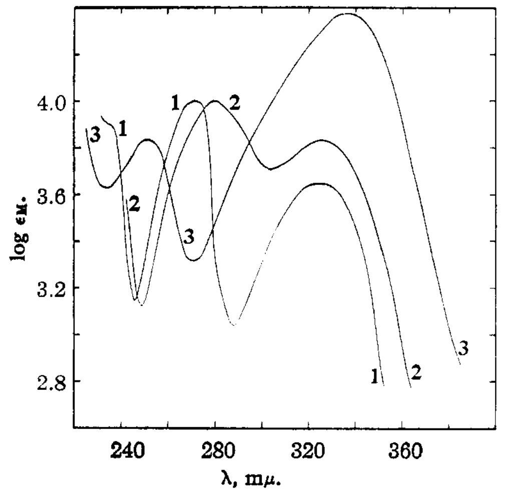

Fig. 4.—Ultraviolet absorption spectra of 2,4-dihydroxy-5-methylacetophenone IV: curve 1, in cyclohexane; curve 2, in 50% ethanol–50% 0.10 N HCl solution; curve 3, in 0.01 N NaOH solution.

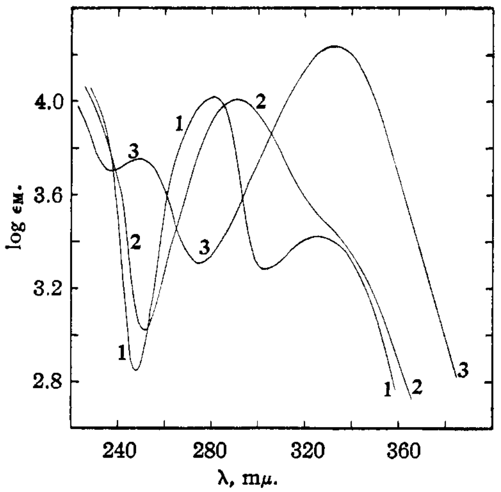

Fig. 5.—Ultraviolet absorption spectra of 2,4-dihydroxy-3,6-dimethylacetophenone VII: curve 1, in cyclohexane; curve 2, in 50% ethanol–50% 0.10 N HCl solution; curve 3, in 0.01 N NaOH solution.

by the procedure of Seshadri,[11] m. p. 155–156° (lit.[11] 156–157°), IX by the procedure of Yanagita,[7] m. p. 138–139° (lit.[7] 138°), X by the method of Desai,[12] m. p. 146–147° (lit.[12] 142–144°), 2,6-dimethoxyacetophenone by the method of Mauthner,[13] m. p. 72–73° (lit.[13] 73–74°), and 2-hydroxy-6-methoxyacetophenone by the method of Limaye,[14] m. p. 58–59° (lit.[14] 60°).

2,6-Dimethoxy-3-methylacetophenone.—To a mixture of 50 mg. of 2,6-dihydroxy-3-methylacetophenone and 3 ml. of methanol was added alternately and dropwise 1 ml. of dimethyl sulfate and 2 ml. of a 20% potassium hydroxide solution, the mixture being kept approximately neutral. When the addition was complete, the mixture was cooled and shaken with water and petroleum ether, the organic layer was washed with water, dried, evaporated to a low volume, and the product was crystallized, wt. 40 mg., m. p. 40–41° (wedge shaped white crystals), negative ferric chloride test. Further recrystallization of the material did not alter its melting point.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.88; H, 7.36.

2,6-Dihydroxy-3,4-dimethylacetophenone.—A mixture of 400 mg. of 4,5-dimethylresorcinol,[6] 226 mg. of acetyl chloride, 1.15 g. of aluminum chloride and 2 ml. of nitrobenzene was allowed to stand at room temperature for one hour, heated to 60°, cooled and poured into a mixture of ice and water. The resulting mixture was extracted with ether, and the ether extract was extracted twice with 1 N alkali. The alkaline extracts were combined, washed with ether, acidified, and the product was extracted into ether, the ether layer was washed with water, dried, evaporated to an oil, and the oil was crystallized from methanol and water; the product was sublimed, and again crystallized from methanol and water, wt. 45 mg., m. p. 82–

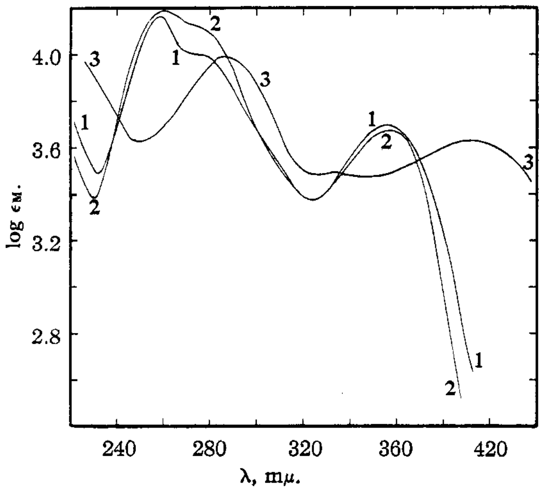

Fig. 6.—Ultraviolet absorption spectra of 2,6-dihydroxy-3,4-dimethylacetophenone XI: curve 1, in cyclohexane; curve 2, in 50% ethanol–50% 0.10 N HCl solution; curve 3, in 0.01 N NaOH solution.

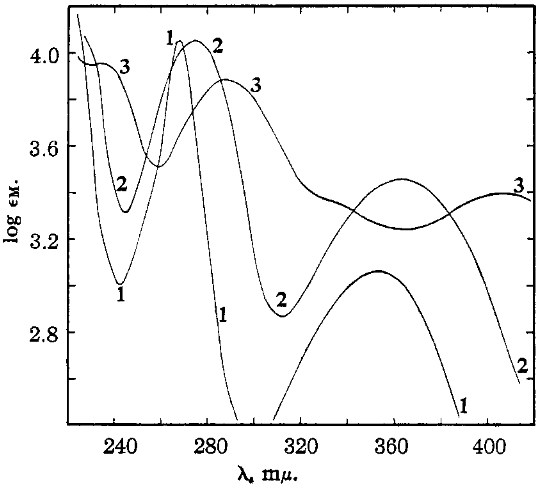

Fig. 7.—Ultraviolet absorption spectra of 2,6-dihydroxy-3,5-dimethylacetophenone XII: curve 1, in cyclohexane; curve 2, in 50% ethanol–50% 0.10 N HCl solution; curve 3, in 0.01 N NaOH solution.

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(11) Rangasuami and Seshadri, *Proc. Indian Acad. Sci.*, **8A**, 214 (1938).

(12) Desai and Vakil, *ibid.*, **12A**, 391 (1940).

(13) Mauthner, *J. prakt. Chem.*, **139**, 290 (1934).

(14) Limaye, *Rasayanam*, **1**, 64–68 (1936).

83° (faintly yellow needles). This material gave a black coloration with an aqueous ferric chloride solution.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.43; H, 6.70.

2,6-Dihydroxy-3,5-dimethylacetophenone.—The compound 2,4-dihydroxy-5-methylbenzaldehyde[15] (m. p. 146–147°, lit.[15] 146–145°) was prepared by formylation of 4-methylresorcinol[6] (yield, 85%), and the product was converted to the dimethyl ether, m. p. 117–118° (lit.[15] 116.5°) in a yield of 87%. This aldehyde was reduced through the use of the Huang modification of the Wolff-Kishner reaction[6] to give a 78% yield of 1,3-dimethoxy-4,6-dimethylbenzene, m. p. 75–76° (lit.[16] 76°). This substance was demethylated with 48% HBr to give a 92% yield of 4,6-dimethylresorcinol, m. p. 127–128° (lit.[16] 124.5–125°). The procedures used for the above transformations are strictly analogous to procedures recorded for similar reactions,[6] and are not duplicated here.

A mixture of 1 g. of 4,6-dimethylresorcinol, 0.75 g. of acetic anhydride and 1 ml. of a 45% solution of boron fluoride-etherate was allowed to stand at room temperature overnight. The yellow needles that separated were collected and boiled with a 50% methanol–50% water solution, cooled, and the needles that separated were recrystallized twice from methanol and water, wt. 200 mg., m. p. 139–140° (yellow needles). This material gave a black coloration with an aqueous ferric chloride solution.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.83; H, 6.92.

Fries Rearrangement of the Diacetate of 4,6-Dimethylresorcinol.—The diacetate of 4,6-dimethylresorcinol (m. p. 44°, lit.[16] 45°) was prepared from the free phenol by the method of Pfaff.[16] A mixture of 1.2 g. of this acetate and 2.4 g. of aluminum chloride was heated to 120° and the temperature was raised to 180° over a period of an hour. The material was then cooled, decomposed in boiling water, and the product was extracted with ether. The ether solution was extracted with a dilute alkaline solution, and this aqueous extract was washed with ether, acidified, and the product was extracted with ether; the ether solution was then washed with water, dried and evaporated to an oil. The oil was dissolved in a small amount of methanol, the solution was treated with charcoal, filtered and the product crystallized by the addition of water. The material that separated was recrystallized from methanol and water to give 210 mg. of faintly yellow needles of 2,4-diacetyl-6-methylresorcinol, m. p. 83–84°.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.40; H, 5.63.

Summary

1. The preparations of 2,6-dihydroxy-3,5-dimethylacetophenone, 2,6-dihydroxy-3,4-dimethylacetophenone and 2,4-diacetyl-6-methylresorcinol are described.

2. The ultraviolet absorption spectra of all possible mono- and di-nuclear methylated derivatives of 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone have been reported. An empirical correlation of the positions of the spectral bands of these compounds has been made.

LOS ANGELES, CALIFORNIA RECEIVED APRIL 23, 1949

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[15] Gattermann, *Ann.*, **357**, 340, 372 (1907).

[16] Pfaff, *Ber.*, **16**, 1138 (1883).

[CONTRIBUTION FROM THE PHYSICS DEPARTMENT, UNIVERSITY OF CHICAGO]

Structures of Complexes Formed by Halogen Molecules with Aromatic and with Oxygenated Solvents[1]

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I. Introduction

It is a familiar fact that iodine forms violet-colored solutions in certain solvents, brown solutions in others. In some solvents, for example benzene and methylated benzenes, it forms solutions of intermediate color. The most usual, although not universally accepted, explanation of the brown solutions has been that the altered color results from formation of molecular complexes.

Recently Benesi and Hildebrand,[1a] using spectroscopic methods, have shown definitely that benzene and mesitylene form 1:1 complexes of considerable stability with iodine. For solutions of iodine in these substances as solvents, they find that 60 or 85%, respectively, of the dissolved iodine is present in the complexes. This work lends support to earlier strong but less conclusive evidence by Hildebrand[1b] and others for the presence of 1:1 complexes in solutions of iodine in alcohol and other "brown" solvents.

On the other hand, the close agreement in form and intensity between the spectrum of iodine in the vapor state and in "violet" solvents (aliphatic hydrocarbons, carbon tetrachloride, etc.) indicates that complexes are not formed in these.[2,3,4] Other evidence[1a] supports this.

In the present paper, the existence of specific 1:1 complexes will be *assumed as established* in all cases except for the "violet" solvents.[5] An at-

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[1] This work was in part assisted by the ONR under Task Order IX of Contract N6ori-20 with the University of Chicago.

[1a] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 2382 (1948); **71**, 2703 (1949).

[1b] Hildebrand and Glascock, THIS JOURNAL, **31**, 26 (1909).

[2] See refs. 1a, 3, 4 and additional references given in refs. 1a, 3.

[3] G. Kortüm and G. Friedheim, *Z. Naturforschung*, **2a**, 20 (1947): comparison of absorption spectra of iodine in vapor, in cyclohexane solution, and in ether solution, from visible to λ2330.

[4] E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 540 (1936): comparative graph of extinction coefficient ε in visible for vapor, vapor plus foreign gas at 50 cm. pressure, and carbon tetrachloride solution; and useful brief survey. By using foreign gas, the usual errors due to band structure below the convergence point of the bands are overcome, and the resulting ε curve is perhaps the most reliable measure available for the vapor. In bromine,[4] foreign gas causes a considerable increase in ε, but internal evidence indicates that this effect is absent in iodine.

[5] Further work will of course be desirable in order to establish the correctness of this assumption as directly as possible for examples of the second and third of the types of complexes considered here.