[CONTRIBUTION FROM THE BAKER CHEMICAL AND THE ROCKEFELLER PHYSICAL LABORATORIES OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF BENZAURIN[1]

BY W. R. ORNDORFF, R. C. GIBBS AND S. ALICE MCNULTY[2]

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For some time we have been making a careful study of the absorption spectra of various organic compounds. As we plan to present additional results in later papers, it is desirable at this time to give a brief outline of our experimental method and procedure and to explain the general arrangement of our results.

The measurements of absorption in the ultraviolet region were made with a Hilger quartz spectrograph, Type E36 and their quartz sector photometer. By placing a suitable quartz bi-prism at the slit of the spectrograph two spectra, one of the light transmitted by a given layer of the solution being studied and the other of the light from the same source transmitted by an equal layer of the solvent used, can be simultaneously photographed in contiguous positions on the plate. Where the blackening of the plate for the two spectra is the same, the ratio of the transmission of the solution to that of the solvent, that is, the transmittance[3] of the solute, is equal to the inverse ratio of the openings of the sectors placed in the two beams. Twelve to fifteen such pairs of spectra, each for a different ratio of sector openings, can readily be obtained on a single plate.

The discharge under water from a Tesla coil was used as the source of light. By placing the electrodes far enough apart so that none of the radiation reaching the plate came from the regions within 3 or 4 mm. from either electrode, a continuous spectrum without any lines characteristic of the material of the electrodes was obtained throughout a wide region of the ultraviolet and well into the green part of the visible spectrum. For use in locating the positions in the spectrum of points in the contiguous spectra where the blackening of the plate was the same, the line spectrum of some metal, usually aluminum, from a spark in air was placed at the top and bottom of each plate. To determine whether the apparatus is in proper alignment, exposures near the top and bottom of each plate, either without any absorbing medium in either beam or with layers of equal thickness of some solvent in both beams, were made. If the two contiguous spectra in both these cases show no inequality of blackening

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[1] The assistance of a grant made to the first two authors from the Heckscher Research Foundation of Cornell University which enabled us to make the measurements described in this report is gratefully acknowledged.

[2] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1921–23.

[3] In using this term we are following a suggestion made in *Bur. Standards Sci. Papers*, **440,** 124 (1922).

for any region of the spectrum, we feel confident that the intermediate exposures through any solution yield reliable information in regard to its absorption.[4]

Whenever a solution exhibited color, its absorption was determined by visual observations made with a Schmidt and Haensch spectrophotometer, equipped with a Lummer and Brodhun contrast prism. These observations often overlapped those made photographically, in which case each served as a check on the other. In both regions of the spectrum our measurements enable us to compensate fully for the loss by reflection which a beam of light undergoes at the surfaces of the container when passing in and out of the solution, and also for the loss due to absorption of the solvent alone, so that we obtain the true transmittance of the dissolved solute.

In preparing the solutions, only the purest substances obtainable have been used. The solutes were first thoroughly dried in a vacuum desiccator, carefully weighed in glass-stoppered weighing bottles and placed in the solvent, whose volume was determined from accurate buret measurements. All solutions were made and kept in Pyrex or hard-glass containers and, whenever preserved, have been kept in a darkened room. Usually a fairly strong solution is first prepared and such dilutions as may be found necessary to determine the absorption over the desired range of the spectrum are then made from this stock solution. It has been our practice to measure the absorption of a solution as soon as possible after it is made up, especially in the case of the dilutions made from the stock solutions.

The cells used for holding the solution and solvent during the measurements are made of Pyrex glass tubes closed at each end with a plate of crystal quartz. The quartz plates are held in place with sufficient mechanical pressure to prevent leakage. Cells of this type are easily cleaned and thus contamination from previously used solutions is prevented. As these cells are placed at some little distance from the slit of the spectrograph it is necessary, in order to eliminate error caused by refraction, to have the tubes of uniform length along all elements and the quartz plates of uniform thickness. It was found by experiment that no change in radiation reaching the photographic plate could be detected when the cell was rotated about its axis if the variation in length of tubes or in thickness of quartz plates did not exceed 0.01 mm. across a diameter of about 20 mm.

The molecular coefficient of absorption, β_m, used as ordinate in plotting the curves is defined by the equation, $\beta_m = (m/c'd) \log (1/T)$, where m is the molecular weight of the solute, c' the concentration of the solution in grams of the solute per liter of solution, d the thickness of the layer in centimeters, and T the transmittance of the dissolved solute, that is, the percentage of the light unabsorbed by the dissolved solute in passing through a layer of solution d cm. thick. The reciprocals of the wave lengths, expressed in millimeters and called frequency numbers, are used as abscissas in plotting the curves.

The location of the points of equal blackening in the contiguous spectra

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[4] A more detailed account of this method of measuring absorption is given by Howe [*Phys. Rev.*, [2] 8, 674 (1916)] and by Gibson and others, *Bur. Standards Sci. Papers*, **440**, (1922).

heretofore referred to has been determined by means of a comparator designed especially for this kind of work.[5]

It has not been found feasible to indicate all of our observations as plotted points. When the observations for various concentrations are expressed in terms of the absorption coefficient, the points are often so crowded together that it is difficult to distinguish them when plotted on a small scale. In selecting the points to be plotted in such cases we have tried to make them as representative as possible. In drawing the curves we have been guided by all of the observations available.

It is often possible by a direct examination of the photographic plate to locate the peaks of broad absorption bands more readily than can be done from the plotted points. It is also possible in this way to detect weak absorption bands which cannot be brought out by merely locating the points of equal blackening. This is especially true when these bands are superimposed upon other and broader bands. In all such cases the location of the peak of the band has been indicated by a short vertical line drawn across the curve.

In order to minimize the chance for error it has been our established practice to make all absorption measurements in duplicate with independent solutions.

In connection with the study of the absorption spectra of the phthaleins and the sulfonephthaleins, which we are making, it was thought highly desirable to determine the absorption curves for benzaurin (phenolbenzein) in neutral, alkaline and acid solution, as benzaurin is the mother substance of the phthaleins and of the sulfonephthaleins. The absorption of benzaurin as reported by previous investigators[6] has been studied in most cases only in the visible.

The benzaurin used in this work was an exceedingly pure product prepared by Dr. H. R. Snow of the University of Michigan to whom we wish here to express our thanks. It was in the form of orange-red crystals, which form a *yellow-orange* solution in absolute ethyl alcohol. The color fades on standing to a *light yellow.* Fig. 1 gives the curves for benzaurin in absolute ethyl alcohol. Curve A represents the absorption of the fresh solution and Curve B the absorption of the same solution after ten days. The band located at frequency number 2300 in the faded solution (Curve B) is only $^1/_{18}$ as intense as it is in Curve A and the other bands at 2902 and 3613 and the very faint one at 3520, all have smaller absorption coefficients than in the fresh solution. By heating the *yellow* (faded) alcoholic solution of benzaurin the original *yellow-orange* color may be restored but it soon fades again.

[5] Tyndall, *Bur. Standards Tech. Papers,* **148** (Appendix) (1920).

[6] Meyer and Hantzsch, *Ber.,* **40,** 3479 (1907). Meyer, *Ber.,* **41,** 2568 (1908). Formanek and Grandmougin, *Untersuch. Nachweis Farbstoffe,* **I,** 126 (1908). Moir, *Roy. Soc. S. Africa,* **7,** 5 (1918).

Our observations, both visual and photographic, fail to give any indication of absorption bands at 2033 and 2174 as reported by Formanek and Grandmougin.[6] The strength of solution used by them is not given. These bands are described as being weak and ill defined. Their presence may have been due to impurities which are absent from the more recently prepared crystalline product. It is not surprising that, working only in the visible, they did not discover the strong band at 2300, the peak of which lies on the boundary between the visible and ultraviolet. R. Meyer and O. Fischer[7] have measured the absorption of fuchsone and benzaurin in alcoholic solutions but their results for the absorption of benzaurin in alcoholic solution seem to be incomplete, since they reported only two bands at frequency numbers 2283 and 3567 (estimated from their curves).

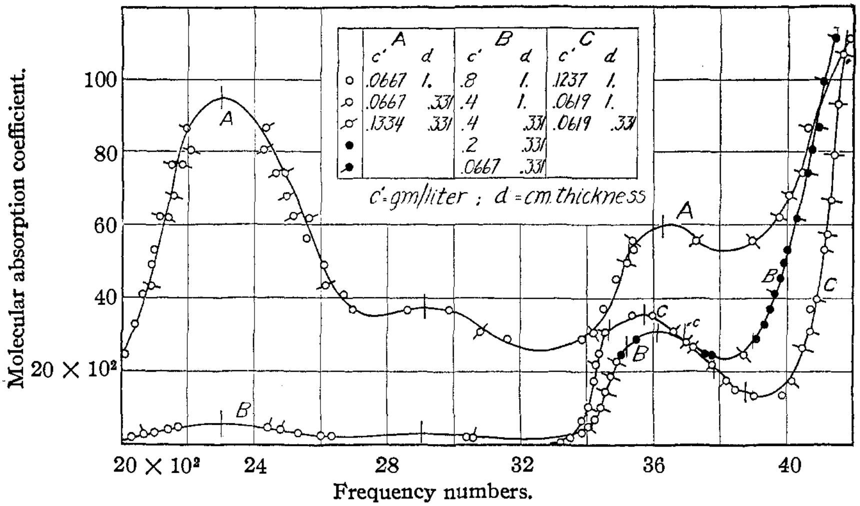
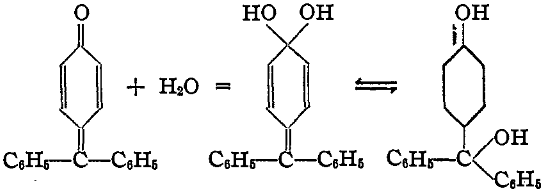


Fig. 1.—*A*. Benzaurin in neutral alcoholic solution. *B*. Solution *A* after standing for 10 days. *C*. Di-*p*-dihydroxy-triphenylmethane in neutral alcoholic solution.

From our work on the absorption spectra of the sulfonephthaleins and on fuchsone and benzaurin, we are inclined to believe that both fuchsone and benzaurin are present in alcoholic solutions in the form of the *quinoid hydrate* and the *carbinol*.



Fuchsone Quinoid hydrate Carbinol

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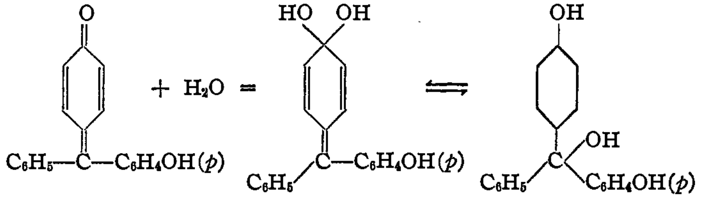
[7] Meyer and Fischer, *Ber.*, **46**, 70 (1913).



Benzaurin (quinoid) Benzaurin, quinoid hydrate Benzaurin, carbinol

Bistrzycki and Herbst,[8] who first made fuchsone, speak especially of the remarkable ease with which it takes up the elements of water and Gomberg[9] has actually isolated both the carbinol and the quinoid hydrate of fuchsone and shown that these substances crystallize together from alcohol and that one may readily be converted into the other. Both fuchsone and benzaurin give the same type of absorption curve, as is to be expected, since benzaurin is *p*-hydroxyfuchsone. The absorption spectra of alcoholic solutions of fuchsone and benzaurin are not due to the presence of the *quinoid* form of these substances, as Meyer and Fischer[7] state but, we believe, to the presence of the *quinoid hydrate* and the carbinol. When the solutions are first prepared, the quinoid hydrate is formed by the assumption of a molecule of water and the *hydrate* gradually goes over to the *carbinol* until equilibrium is established, after the solutions have stood for ten days. This solution then is a *light yellow* because it contains a large quantity of the colorless carbinol and only a small amount of the *colored* hydrate. When this *yellow* solution is heated some of the carbinol is converted into the hydrate and the original color is restored. In accord with this view is the fact that the type of curve for the *fresh* solution of benzaurin and for the same solution after it has *faded* is the same and that the peaks of the four bands are located at practically the same frequency numbers. This means, we think, that a change in the equilibrium between the *colored quinoid hydrate* and the *colorless carbinol* is taking place.

From measurements made on an independent solution after it had faded we are convinced that equilibrium is approximately reached within 24 hours after the solution is made. That the solution is fading quite rapidly when first made up is indicated by the fact that in the band at 2300 the points for $c' = 0.0667$ g./liter lie consistently above those for $c' = 0.1334$ g./liter. In the normal course of photographing, an interval of about two hours occurred between exposures for these two concentrations.

Curves A and B, Fig. 2, show the effect of adding different amounts of hydrochloric acid to the alcoholic solution of benzaurin. The type of the curve is entirely different from that of benzaurin in alcohol alone. When hydrochloric acid is added to the alcoholic solution of benzaurin an ***orange*** color develops. With the ratio of 155 molecules of hydrochloric acid to

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[8] Bistrzycki and Herbst, *Ber.*, **36,** 2337 (1903).

[9] Gomberg, THIS JOURNAL, **35,** 1035 (1913).

one of benzaurin, two new bands develop at frequency numbers 1985 (entirely in the visible) and 2490. The addition of more acid intensifies these bands and brings out the band at 3760 and a weak shoulder in the vicinity of 3450. This change in the absorption spectrum produced by the addition of hydrochloric acid is due, we believe, to the formation of benzaurin hydrochloride. Benzaurin has basic as well as acid properties. Baeyer[10] has actually made benzaurin sulfate. The addition of the acid causes the carbinol to go over to the quinoid hydrate, which splits off water and forms the colored, quinoid benzaurin hydrochloride, the absorption of which is represented by Curve B. Curve A represents the transition stage in the formation of the hydrochloride. In the region of higher frequency numbers this curve resembles that for the faded neutral alcoholic solution, Curve B, Fig. 1. The two bands at 3520 and 3613 in the faded neutral solution still persist, their position in the slightly acid solution having been determined as 3520 and 3626, while there is the beginning of a new band at 3760, which becomes very prominent in the more concentrated acid solution.

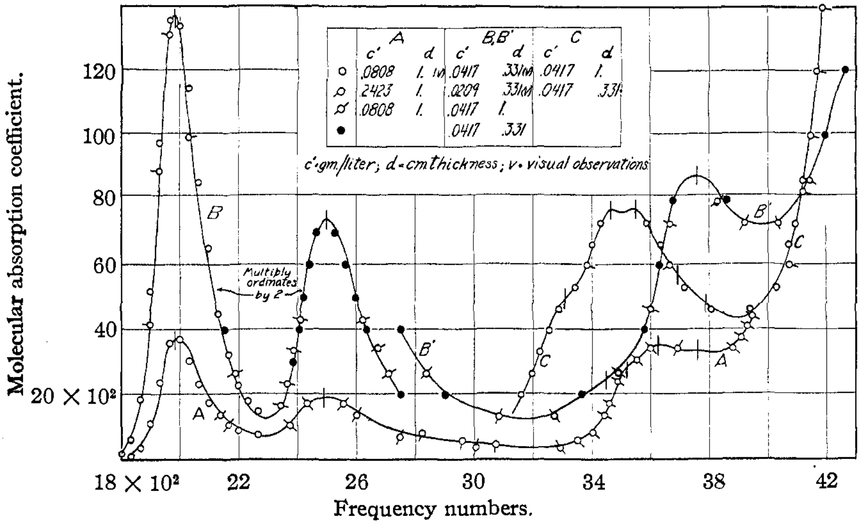

Fig. 2.—Benzaurin in alcoholic HCl solution. *A*. 1 mole:155 moles of HCl. *B*. 1 mole:17,400 moles of HCl. *C*. Solution *B* after standing for one week.

After Solution B had stood for one week it became *colorless* and Curve C represents its absorption. This curve C is very similar to Curve C in Fig. 1, representing the absorption of the reduction product of benzaurin, di-*p*-dihydroxytriphenyl-methane in absolute ethyl alcohol. It is interesting to note that four of the five bands[11] (3465, 3571, 3695 and 3782) of this

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[10] Baeyer, *Ber.*, **36**, 2774 (1903).

[11] Solutions of di-*p*-dihydroxytriphenyl-methane containing as much as 31.69 g. per liter failed to reveal any additional absorption bands for frequency numbers smaller than 3400.

substance occur in about the same positions as those obtained for the *colorless* alcoholic acid solution of benzaurin. The change of the *colored* alcoholic acid solution of benzaurin to the *colorless* solution is due to the reducing action of alcohol and hydrochloric acid on the benzaurin. Kauffmann and Pannwitz[12] have shown that the action of hydrochloric acid and alcohol is quite a general reaction for reducing the triaryl carbinols to hydrocarbons, and the similarity of Curves C in Figs. 1 and 2 would seem to show the presence either of the reduced form of benzaurin, di-*p*-dihydroxytriphenylmethane, or of the diethyl ether of this reduced compound or possibly of a mixture of the two; that is, that the alcoholic hydrochloric acid not only reduces the benzaurin to dihydroxytriphenylmethane but also forms the diethyl ether.

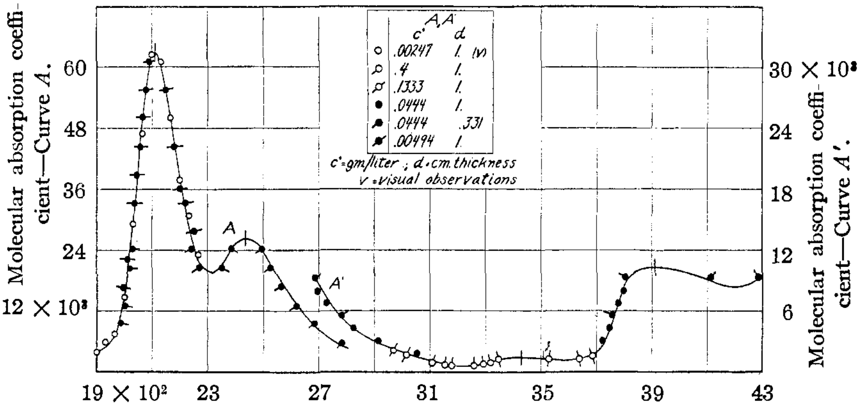

Fig. 3.—Benzaurin in concd. (93%) sulfuric acid.

Fig. 3 gives the curve for the solution of benzaurin in 93% sulfuric acid. The type of curve is very similar to Curve B in Fig. 2 representing 17,400 molecules of hydrochloric acid to one of benzaurin in alcohol. This curve undoubtedly represents the absorption due to the formation of benzaurin sulfate, just as Curve B in Fig. 2 represents the absorption due to the formation of benzaurin hydrochloride. The band at 2112 is entirely in the visible region; the four others are in the ultraviolet part at 2437, 3430, 3507 (very weak) and 3910. The bands at 2112 and 2437 are twice as intense as the corresponding bands in Curve B in Fig. 2. This is probably due to the more complete conversion of the benzaurin into the sulfate in the concd. sulfuric acid solution.

Fig. 4 shows the effect of adding increasing amounts of alkali to the alcoholic solution of benzaurin. The similarity of these curves to those in which acid is added to the benzaurin solution should be pointed out. In both cases we believe that the change is brought about by the conversion

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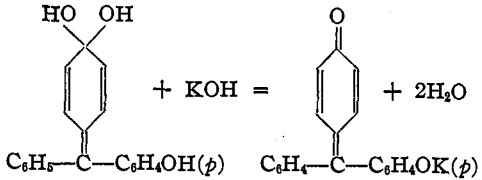
[12] Kauffmann and Pannwitz, *Ber.*, **45**, 766 (1912).

of the carbinol to the colored, quinoid hydrate and this by the loss of water forms the quinoid potassium salt of benzaurin, or in the case of the acid,



Benzaurin, quinoid hydrate

Potassium salt of benzaurin, quinoid

a benzaurin salt of the acid as already shown. Attention should be called to the similarity of the absorption curves given by Meyer and Fischer[7] in their Fig. 2, for benzaurin in alkaline solution and for Döbner's violet in alcohol containing hydrochloric acid. A comparison of the two structural formulas shows that both contain the *quinoid* group and it would hence appear that *this group alone* is the cause of the *absorption* and *color* of these compounds.

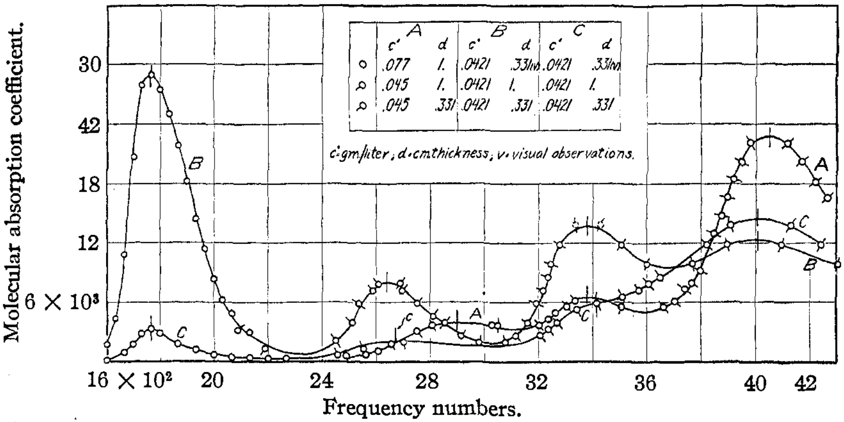
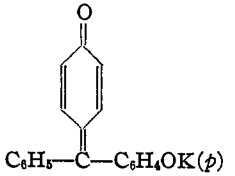
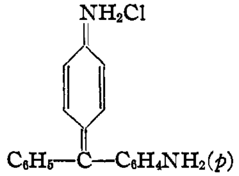


Fig. 4.—Benzaurin in alcoholic KOH solution. *A*. 1 mole:1.2 moles of KOH. *B*. 1 mole:18 moles of KOH. *C*. 1 mole:60 moles of KOH.



Potassium salt of benzaurin



Döbner's violet (HCl)

In Fig. 5 is shown the absorption curve of the *colorless* solution of benzaurin in 33% aqueous potassium hydroxide (Curve A) and of benzaurin in 60 molecular equivalents of alcoholic potassium hydroxide (Curve B). Curve C gives the absorption of the solution used in B after it had stood one week and the color had almost disappeared. The absorption in the ultraviolet of the colorless, alkaline (33% potassium hydroxide) solution of benzaurin is undoubtedly due to the presence of the colorless dipotassium salt of the carbinol, and it will be seen from an examination of Curve C that it is the formation of this dipotassium salt of the carbinol which causes the solution used in obtaining Curve B to fade after one week.

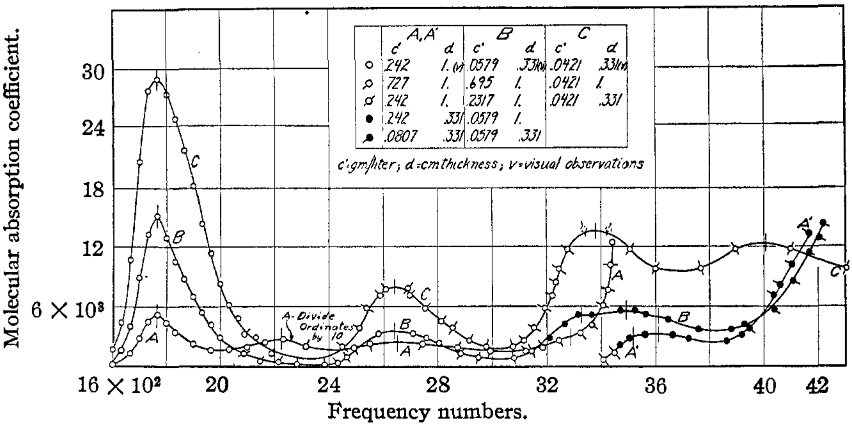
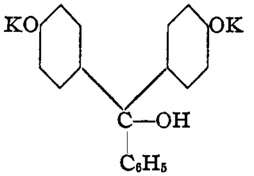


Fig. 5.—*A*. Benzaurin in aqueous 33% KOH solution. *B*. Benzaurin—1 mole:60 moles of KOH in alcohol. *C*. Solution *B* after standing for one week.



Dipotassium salt of the
carbinol (colorless)

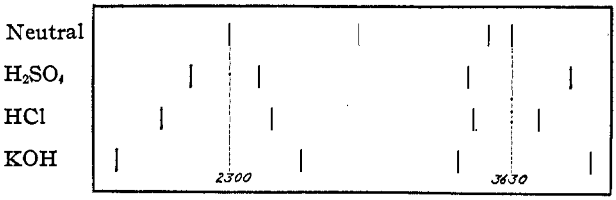


Fig. 6.—Relative position of absorption bands of benzaurin in neutral, acid and alkaline solution.

It is interesting to note that four absorption bands are found in both the sulfuric and hydrochloric acid solutions and in the alkaline solutions and that none of these four bands coincides with any of the bands found in the neutral solution. The relative positions of the peaks of all these bands are shown in Fig. 6.

The bands in the acid and alkaline solutions are grouped in two pairs about the two more intensive bands of the neutral solution located at frequency numbers 2300 and 3630. It is often possible, especially when we are dealing with fairly strong bands, to bring out the acid or alkaline bands along with the intermediate band of the neutral solution by using solutions containing a small amount of acid or of alkali; that is, by gradually increasing the acid or alkali content of a solution the new bands increase in intensity without any shift in their position while the band characteristic of the neutral solution decreases in intensity. This gradual transition from one type of absorption to the other has been found to be even more striking in the case of certain other substances which we have studied.

TABLE I

FREQUENCY NUMBERS OF ABSORPTION BANDS

	Substance	Frequency No.					
1.	Benzaurin in neutral abs. alcohol	2300	2913	3526	3630		
1a.	Same solution 10 days later	2300	2902	3520	3613		
2.	Di-*p*-dihydroxytriphenylmethane in neutral abs. alcohol	3465	3571	3695	3782	3877	
3.	Benzaurin (1 mol.): 155 mols. of HCl in abs. alcohol	1985	2490	3520	3626	3760	
4.	Benzaurin (1 mol.): 17,400 mols. of HCl in abs. alcohol	1985	2500	3450 (approx.)		3760	
4a.	Same solution one week later	3308	3463	3549	3693	3788	
5.	Benzaurin in 93% H_2SO_4	2112	2437	3430	3507[a] (approx.)	3910	
6.	Benzaurin (1 mol.): 1.2 mols. of KOH in abs. alcohol	1765	2226	2650	3290	3515	3610
7.	Benzaurin (1 mol.): 18 mols. of KOH in abs. alcohol	1765	2640	3327	3495	3610	
8.	Benzaurin (1 mol.): 60 mols. of KOH in abs. alcohol	1765	2640	3380	4005		
8a.	Same solution one week later	1765	2674	3415	4005		
9.	Benzaurin in 33% KOH (aqueous)	2900	3380	4050			

[a] The existence of this band is somewhat doubtful.

We are much indebted to Mr. C. V. Shapiro for assistance in drawing our curves.

Summary

1. The experimental method used in measuring absorption spectra and the precautions taken to insure accurate and reliable data have been outlined.

2. Curves showing the absorption spectra of solutions of benzaurin in neutral alcohol, alcoholic hydrochloric acid, 93% sulfuric acid, alcoholic alkali and 33% aqueous alkali and of di-*p*-dihydroxytriphenyl-methane in neutral alcohol have been recorded and discussed.

3. It has been suggested that the absorption spectra of benzaurin in neutral alcohol are due to the presence of a quinoid hydrate form of benzaurin, in acid solutions to a benzaurin salt of the acid, in the alkaline (potassium hydroxide) solution to the quinoid potassium salt of benzaurin, and in the strongly alkaline (33% potassium hydroxide) solution to the dipotassium salt of the carbinol.

4. A table showing the positions of maximum absorption, expressed in frequency numbers, for all the bands in each of the solutions studied has been prepared.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

KETENES IN THE FRIEDEL AND CRAFTS REACTION

BY CHARLES DE WITT HURD

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In recent years, two modifications of the Friedel and Crafts reaction have received prominence because of their successful application. In one of them[1] it has been demonstrated that ethylene, with high-speed stirring, may be used instead of ethyl halides for the attachment of ethyl groups to an aromatic nucleus. In the other it has been found that acid anhydrides[2] may be used quite generally instead of acid chlorides for the production of aromatic ketones. The use of acetic anhydride in particular was emphasized.

From a theoretical standpoint, it is but a short step from acetic anhydride to ketene. Both compounds generate acetic acid on the addition of water, and thus both compounds may be considered as anhydrides of acetic acid. The similarity of the two compounds made it natural to wonder whether or not ketene would also be a successful reagent in the Friedel and Crafts reaction. It was considered probable that the greater reactivity of ketene might offset the disadvantage of immiscibility, due to the fact that ketene is a gas. There was a likelihood, also, that one molecular proportion of aluminum chloride might suffice. With acetic anhydride, two molecular proportions are necessary.

From the results of this investigation, it will be seen that ketene does react with various types of aromatic nuclei with the resultant production of ketones. Benzene and anisole were the first compounds studied. Reaction occurred readily even when the reaction vessel was surrounded by an ice-bath. The progress of the reaction was not a simple one, however, inasmuch as a complex mixture of substances invariably resulted. Acetophenone and methoxyacetophenone were undoubtedly formed, as

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[1] Milligan and Reid, THIS JOURNAL, **44**, 206 (1922); *Ind. Eng. Chem.*, **15**, 1048 (1923).

[2] Noller with Adams, THIS JOURNAL, **46**, 1889 (1924).