had been effected. Subsequent to hydrolysis by pouring into water, the ether layer was separated and then dried, and the ether removed by distillation. The residual orange colored oil was heated at 190° for one-half hour with 40 cc. of nitrobenzene to oxidize the intermediate 2-(*p*-aminophenyl)-1,2-dihydroquinoline. Then by distillation under reduced pressure (0.5 mm.) the excess nitrobenzene, unreacted quinoline and 2-*n*-butylquinoline were removed. Further distillation gave 17.5 g. [70% (based on 70% halogen–metal interconversion)][12] of a heavy, viscous orange-colored glassy product which came over in the range 180–190° (0.003 mm.).

This glass was dissolved in hot 95% ethanol, and to the solution was added 55 g. of picric acid in boiling ethanol. After refluxing for 15 minutes, there was obtained 30 g. of mixed picrates which melted over the range 170–190°; and recrystallization from an acetone–95% ethanol mixture gave a m. p. of 188–190°. After extracting 22 g. of the picrates in a Soxhelt extractor with benzene, there remained 20 g. of an orange picrate melting at 194–195°; and from the benzene extract there was obtained 1.8 g. of a yellow picrate melting at 200–210°.

The base, liberated from the orange picrate by dil. ammonium hydroxide, gave 6 g. (33%) of 2-(*p*-aminophenyl)-quinoline which showed no depression in a mixed melting point determination with an authentic specimen prepared by another procedure.[15] The picrate of the authentic specimen was shown to melt at 197–198°, and there was no depression in melting point on admixture with the picrate obtained from the RLi product.

The yellow picrate was decomposed by boiling ammonium hydroxide solution to give a colorless crystalline compound which melted at 148–148.5° after charcoaling and crystallizing from benzene. This compound may be 2-(*n*-butyl)-2-(*p*-aminophenyl)-1,2-dihydroquinoline formed by addition of the lithium salt of *p*-aminophenyllithium to 2-*n*-butylquinoline.[16]

Anal. Calcd. for $C_{19}H_{22}N_2$: N, 10.08. Found: N, 9.60 and 9.75.

The yellow picrate was re-formed by treating a 95% ethanolic solution of the supposed 2-(*n*-butyl)-2-(*p*-aminophenyl)-1,2-dihydroquinoline with a hot ethanolic solution of picric acid. It melted at 220–221° after recrystallization from methyl cellosolve.

Anal. Calcd. for $C_{25}H_{25}O_7N_5$: N, 13.78. Found: N, 13.02 and 13.20.

2-(*p*-Salicylideneaminophenyl)-quinoline.—A mixture of 1 g. (0.0045 mole) of 2-(*p*-aminophenyl)-quinoline and 0.6 g. (0.149 mole) of salicylaldehyde was heated for four hours in a bath held at 150° to give a quantitative yield of product melting at 185–186° after removing the excess salicylaldehyde by washing with 95% ethanol. The sample for analysis melted at 188–188.5° after crystallization from methyl cellosolve.

Anal. Calcd. for $C_{22}H_{16}ON_2$: N, 8.65. Found: N, 8.74.

Summary

2-Phenylquinoline adds phenyllithium to the azomethine linkage to give 2,2-diphenyl-1,2-dihydroquinoline. The general course of this reaction was established by showing that 2-phenyl-2-(*p*-tolyl)-1,2-dihydroquinoline is formed from 2-phenylquinoline and *p*-tolyllithium as well as from 2-(*p*-tolyl)-quinoline and phenyllithium.

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[15] John, *J. prakt. Chem.*, [2] **133**, 13 (1932), and [2] **139**, 97 (1934).

[16] 2-(*n*-Butyl)-quinoline might be expected as a consequence of the prompt addition of any excess of *n*-butyllithium to quinoline.

AMES, IOWA RECEIVED DECEMBER 9, 1946

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

The Absorption Spectra of Some Benzene Derivatives with Unsaturated Side Chains

BY TOD W. CAMPBELL,[1] SEYMOUR LINDEN, SYLVIA GODSHALK AND WILLIAM G. YOUNG

Jones[2] has pointed out that there has been but little work done on the absorption spectra of benzene derivatives with unsaturated side chains, particularly compounds of the type $C_6H_5C{=}C{-}C{-}$, where the double bond is in conjugation with the benzene ring. Since work is being done in these Laboratories on the reactions of cinnamylmagnesium chloride, and of the sodium derivative of allylbenzene,[3] which may result in the production of allylic isomers, in which the double bond is either in conjugation or out of conjugation with the benzene ring, it was deemed of interest to study the absorption spectra of a number of compounds of these types.

Sufficient differences appear in the spectra of the compounds studied to make possible a rapid estimation of the composition of a mixture of allylic isomers, provided the spectra of one or both of the pure compounds can be obtained. Furthermore, the nature of a single reaction product, when only one product is obtained,[4] can be determined.

At present, an attempt is being made to elucidate the structure of allylic Grignard reagents[4] by means of their absorption spectra.

Experimental

The spectra reported here were determined by means of the Beckmann quartz photoelectric spectrophotometer. The solvent used was in all cases 95% ethyl alcohol. The compounds examined were either Eastman Kodak Co. white label preparations, which had been redistilled or recrystallized once, or laboratory preparations which had been thoroughly purified by standard methods. Some of the latter group of compounds required special synthetic procedures, which will be discussed in forthcoming publications. It should be noted that the spectra of a number of these compounds appear in the literature[5]; however they were repeated, in order that uniform data could be presented.

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[1] Abbott Laboratories Research Fellow, 1944–1945.

[2] R. Norman Jones, *Chem. Rev.*, **32**, 1–45 (1943).

[3] (a) Young, Ballou and Nozaki, THIS JOURNAL, **61**, 12 (1938); (b) Campbell and Young, *ibid.*, **69**, 688 (1947); (c) Young and Campbell, unpublished results.

[4] For a discussion of the reactions of allylic Grignard reagents, see Young and Roberts, THIS JOURNAL, **68**, 1472 (1946), and preceding papers in this series.

[5] See reference (2), and the "International Critical Tables."

TABLE I

CHARACTERISTIC MAXIMA, MINIMA AND INFLECTION POINTS IN THE ABSORPTION SPECTRA OF CERTAIN COMPOUNDS

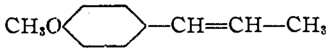
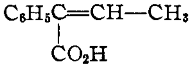
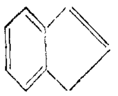
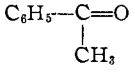
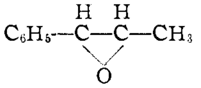
	Compound	Maxima	$\epsilon_{max.}$	Minima	$\epsilon_{min.}$	Inflection pts.,	$\epsilon_{Inf.}$
1	C_6H_6	268	9	267	7		
		261	143	259	47		
		254.5	208	252.5	60		
		249	153	245.5	55		
		243	96	241	43		
		239	54	236	28		
		234	34	228	14		
2	$C_6H_5CH_3$	269	156	267	75	250	95
		265	127	264	125		
		262	190	257	133		
		256	141	228	10		
3	$C_6H_5CH_2OH$	268	90	267	85	243	83
		264	138	263	123		
		258.5	185	254.5	140		
		252.5	155	249	115		
		248	117	229	23		
4	$C_6H_5CH_2Cl$	266	219	263	203		
		260	247	256	200		
		254	208	245	175		
		218	6800				
5	$C_6H_5CH_2CH_2CH_2Br$	268	176	266.5	137		
		264.5	188	263.5	177		
		261	232	260.5	229		
		259	240	256	196		
		253.5	215	250	167		
		248	172	243.5	136		
		242.5	137	238.5	118		
		237	119	235	115		
6	$C_6H_5CH_2CO_2H$	264.5	132	262.5	95		
		258.5	176	255.5	117		
		252.5	142	249	103		
		247.5	107	244	93		
7	$C_6H_5CH_2CH{=}CH_2$	268	176	267	139		
		265	187	264	185		
		262	237	261	234		
		259	240	257	213		
		254	219	232	68.2		
8	$C_6H_5CH{=}CH{-}CH_3$	293	642	290	442		
		284	1030	280	909		
		249	14710	223	4540		
9		258	20350	228	2520	290	2280
10	$C_6H_5CH{=}CH{-}CH_2OH$	292	1625	289	1355		
		283	1955	280	1412		
		250	17050	222	3750		
11	$C_6H_5CH{=}CHCH_2Cl$	293	1070	290	914	283	2200
		254	13910	224	2630		
12	$C'_6H_5CH{=}CHCH_2{-}C(C_6H_5)_2OH$	294	1097	290	800		
		284	1908	282	1761		
		254	20500	229	8540		
13	$C_6H_5CH{=}CHCO_2H$	282	19930	230	1870		
		222	14500				
14	 $C_6H_5C(CO_2H){=}CH{-}CH_3$	None		None		254	2505
						228	5840

TABLE I (*Concluded*)

	Compound	Maxima	$\epsilon_{max.}$	Minima	$\epsilon_{min.}$	Inflection pts.,	$\epsilon_{inf.}$
15	$C_6H_5CH{=}CHCH_2CH_2CO_2H$	293	791	290	528		
		283	1120	280	962		
		250	18470	224	4830		
16	$C_6H_5CH{=}CHCH_2C(CH_3)_2CO_2H$	293	978	290	607		
		284	1380	280	1190		
		252	19030	224	4470		
17		280	478	277.5	397	290	140
		249	9340	230	3790	285	243
						220	9340
18	 $C_6H_5{-}\underset{CH_3}{\underset{\vert}{C}}{=}O$	280 (Very broad)	1030	268	850		
		241	13300	216	1710		
19		247 (Very broad)	526	235	420		
		217	8000				

Discussion

Considering toluene as a standard for comparison, Figs. 1 and 2 and the data of Table I indicate that the presence of a double bond not in conjugation with the benzene ring does not affect the absorption spectrum to any appreciable extent (see toluene and allylbenzene, Fig. 1). The presence of a chloride or hydroxyl group on the α-carbon of toluene also does not create any marked change in spectrum (see Table I, toluene, benzyl alcohol and benzyl chloride). In general, the simple monoalkyl benzenes[6] exhibit several maxima between 280 and 240 of low intensity (ϵ = 10–300).

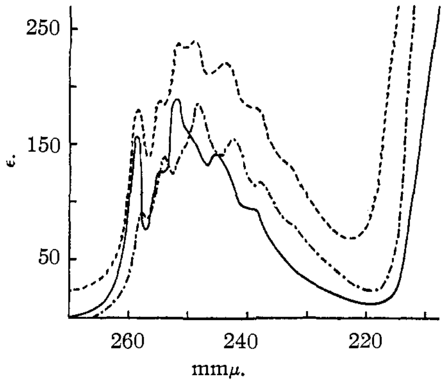


Fig. 1.—Absorption spectra of toluene, —; benzyl alcohol, —·—·—·—, and allylbenzene, - - - - -.

When, however, a carbon–carbon double bond is conjugated with the benzene ring, the absorption spectrum takes on an entirely different character. The fine structure is lost, and the number of maxima reduced (compare allylbenzene and propenylbenzene, Figs. 1 and 2). The absorption is extended to higher wave lengths with characteristic maxima or inflections (ϵ *ca.* 1000) at 293 and 284 mμ. Probably the most striking difference between conjugated and unconjugated alkyl substituted benzene derivatives is that the former exhibits a maximum at about 250 mμ with an extremely high intensity (ϵ = 10,000–20,000). Thus, in the region of 250 mμ a substituted benzene ring with a conjugated double bond absorbs with an intensity fifty to a hundred times greater than the corresponding unconjugated or saturated derivative.

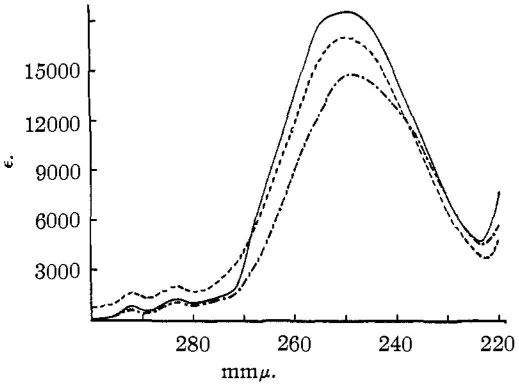


Fig. 2.—Absorption spectra of $C_6H_5CH{=}CHCH_3$, —·—·—·—; $C_6H_5CH{=}CHCH_2OH$, - - - -, and $C_6H_5CH{=}CHCH_2CH_2CO_2H$, —.

Similar observations have been reported by Ramart-Lucas and Amagat,[7] who have compared the spectra of allylbenzene and propenylbenzene, as have Hillmer and Schorning.[8] The latter have also studied some nuclearly substituted benzene derivatives with unsaturated side chains. However, they failed to report the critical maxima between 300 and 280 mμ, which should be present in the spectrum of propenylbenzene. The positions of some of their maxima are also questionable.[9]

To observe the effect of a carbonyl double bond conjugated with a benzene ring, the spectrum of

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(6) Pestemer and Gübitz, *Monatsh.*, **64**, 426 (1934).

(7) P. Ramart-Lucas and P. Amagat, *Bull. soc. chim.*, **51**, 965 (1932).

(8) Hillmer and Schorning, *Z. physik. Chem.*, **167**, 407 (1933).

(9) Compare with Hibbert and Patterson, THIS JOURNAL, **65**, 1862 (1943).

acetophenone was taken. The spectrum is similar, and the intensity of absorption is of the same order as is exhibited by benzene derivatives with carbon–carbon double bonds conjugated with the benzene ring.

The absorption spectrum of α-phenylpropene oxide is very interesting. There is a marked similarity between its spectrum and that of acetophenone (see Fig. 3). The main differences seem to be that the intensity of both maxima of the oxide are about one-half of those of acetophenone, and that the maxima are shifted about 30 mμ lower. It appears obvious, however, that considerable conjugation exists between the benzene ring and the oxide grouping.[10] This is readily shown by further comparison with benzyl alcohol.

Care must be exercised in assigning structure to an unknown substance on the basis of spectra alone, since certain substituents (either on the ring or on the side chain) affect the characteristic spectra markedly. This may be seen from the data for anethole (9, Table I), methylatropic acid (14), which has a carboxyl group in conjugation with the double bond in the side chain, and cinnamic acid (13), with the carboxyl group in conjugation both with the double bond in the side chain and with the benzene ring. However, despite the shift in position (or disappearance) of the characteristic maxima, conjugation is indicated by the high order of the extinction coefficients.

The cyclic compound indene (Fig. 3 and Table I) also differs from the corresponding open-chain compound, propenylbenzene; however, the characteristic high maximum at 249 mμ is present.

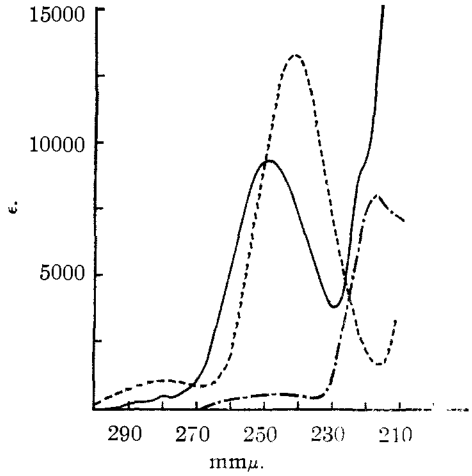

Fig. 3.—Absorption spectra of indene, —; acetophenone - - - -; and α-phenylpropylene oxide, —·—·—.

Our results are in agreement with those of Ramart-Lucas and Hoch,[11] who compared the absorption spectra of indene and its open-chain analog, *o*-methylstyrene.

Summary

1. The absorption spectra of a number of unsaturated benzene derivatives have been studied and compared with the spectra of similar saturated derivatives.

2. It has been found that a double bond in conjugation with the benzene ring produces a very characteristic spectrum, by which this type of compound may be differentiated from saturated derivatives, and from unsaturated compounds without the double bond in conjugation.

LOS ANGELES, CALIFORNIA RECEIVED DECEMBER 3, 1946

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(10) Klotz [THIS JOURNAL, **66**, 88 (1944)] has presented spectroscopic evidence of a similar nature for conjugation between a cyclopropane ring and a carbonyl group or a carbon–carbon double bond.

(11) P. Ramart-Lucas and M. J. Hoch, *Bull. soc. chim.*, [5] **2**, 327 (1935).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

The Electrical Conductivities of Aqueous Solutions of Mixtures Containing Alkylammonium Chlorides

BY A. W. RALSTON AND C. W. HOERR

The many studies which have been made upon homologous series of colloidal electrolytes clearly show the gradation in conductivity behavior which accompanies progressive increases in the chain lengths of the various members. Increase in the chain length of colloidal electrolytes of similar structure is attended by lowered equivalent conductivities of their aqueous solutions and by a shifting of the critical point for micelle formation toward a lower concentration of electrolyte. An example of this effect is found in the conductivity behavior of aqueous solutions of the alkylammonium chlorides,[1] and it has recently been found that in compounds of comparable structures, the chain length is determinative as regards the critical point for micelle formation.[2] Although the conductivity behavior of individual members of various series of colloidal electrolytes has been the subject of many studies, the conductivities of aqueous solutions of mixtures of homologous electrolytes have not been investigated. It has been assumed that the micelles formed in a solution of a specific colloidal electrolyte are of approximately uniform size, the size depending upon the nature of the electrolyte, the concentration, the temperature, and other factors. Where the

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(1) Ralston and Hoerr, THIS JOURNAL, **64**, 772 (1942).

(2) Unpublished observations.