

2,2-Dichloroethanol by Reduction of 2,2-Dichloroacetyl Chloride.—A one-liter three-necked flask fitted with a reflux condenser, mercury sealed stirrer and dropping funnel was charged with 275 ml. of rigorously dried ether. To this was added 13.6 g. (0.36 mole) of pulverized lithium aluminum hydride (20% excess). Stirring produced a milky suspension. After fifteen minutes the addition of 88.6 g. (0.60 mole) of 2,2-dichloroacetyl chloride was begun and continued at a rate determined by the refluxing of the ether. Two hours and a half was required for the addition, vigorous stirring being maintained throughout the addition and for thirty minutes thereafter.

Excess hydride was destroyed by dropwise addition of water while the flask was cooled in a water-bath. Considerable heat was evolved and a white curdy precipitate, presumed to be aluminum hydroxide, was formed. Hydrolysis of the intermediate was effected by the addition of 500 ml. of 10% sulfuric acid.

The pale yellow ether layer, combined with two ether extracts of the aqueous layer, was dried over anhydrous magnesium sulfate, the ether removed by distillation at reduced pressure and the organic residue fractionated

under vacuum through an 18' column packed with glass helices. The fraction collected between 37° and 38.5° (6 mm.) amounted to 44 g. or 63%. At 739 mm. pressure this boiled at 145° (Heilbron lists 146°, pressure unknown).

Analysis for chlorine was carried out by the Rauscher method.³

Anal. Calcd. for $C_2H_4Cl_2O$: Cl, 61.7. Found: Cl, 61.2, 61.3.

Summary

The three chloroacetic acids, their esters and acid chlorides are reduced smoothly by lithium aluminum hydride, the principle product in most cases being the chloroalcohol. The method is recommended as a procedure for the synthesis of 2,2-dichloroethanol.

(3) Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **9**, 296 (1937).

BUFFALO, N. Y.

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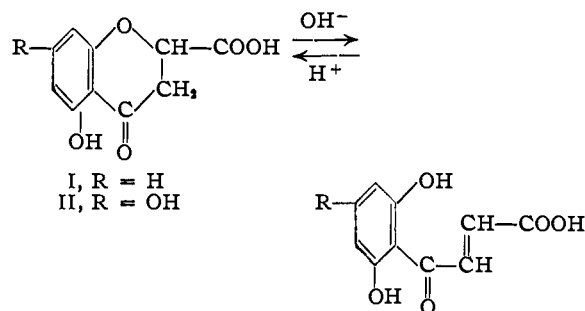
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE VICK CHEMICAL COMPANY]

Ultraviolet Absorption Study of Some Substituted β -Aroylacrylic Acids and 2-Carboxy- γ -chromones and Chromanones

BY CHARLES I. JAROWSKI¹ AND GLENN B. HESS¹

In the preceding paper evidence was presented for the assignment of the 2-carboxy-5,7-dihydroxy- γ -chromanone structure to the acid obtained by the acylation of phlorglucinol with maleic anhydride. Arguments were also set forth to indicate that alkaline hydrolysis of 2-carboxy-5-hydroxy- γ -chromanone followed by acidification resulted in the formation of the corresponding acid.²

A study of the ultraviolet absorption of some 2-carboxy- γ -chromones, 2-carboxy- γ -chromanones and β -aroylacrylic acids was initiated in order to add more evidence in favor of the structures postulated. Furthermore it was of interest to determine if the following chalcone- γ -chromanone type of equilibrium did occur with the two acids studied



for it was quite possible that alkaline hydrolysis of the ethyl ester of I had opened the γ -chromanone ring but that acidification resulted in cycliza-

tion of the desired β -(2,6-dihydroxybenzoyl)-acrylic acid to give the closed structure.

Some chromophorically related compounds were likewise included in order to gain a better insight into the structural features accounting for the characteristic bands observed.

Experimental

The compounds listed in Table I were previously prepared in this Laboratory by methods already described in the literature.

Absorption Measurements.—Absorption determinations were made on a Beckmann Model DU Quartz spectrophotometer, using 1 cm. cemented quartz cuvettes and a hydrogen discharge lamp as the light source. Samples were made up in the range of 0.1% w./v. and dilutions to 0.01 and 0.001% were made with the same solvent. Samples which were run in 0.05 *N* alcoholic potassium hydroxide were made up to a concentration of 0.1% w./v. and dilutions were made with alcoholic potassium hydroxide.

All samples except β -mesitoylacrylic acid followed Beer's law in the concentrations used. β -Mesitylacrylic acid gave anomalous results in the range from 250–300 millimicrons in the shift from 0.001 to 0.01% concentration. Results shown in this range are the absorptions for the 0.01% solution.

Discussion of Results

In Fig. 1 are shown the absorption curves obtained by plotting $\log \epsilon$ as a function of the wave length expressed in $m\mu$. The groups of curves have been displaced vertically by one $\log \epsilon$ unit.

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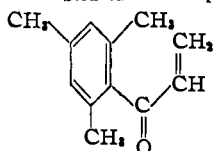
(2) Jarowski, Moran and Cramer *THIS JOURNAL*, **71**, 944 (1949).

TABLE I

Curve	Number	Structure of compound	MAXIMA, MINIMA AND LOG ϵ VALUES FOR THE COMPOUNDS STUDIED					
			Ref.	Solvent	λ_{\max} .	Log ϵ	λ_{\min} .	Log ϵ
5	I		1	95% EtOH	274	3.94	243	3.15
					351	3.48	302	2.81
6	I		2	KOH-EtOH	243	4.07	264	3.52
					282	3.84	310	2.56
					382	3.75		
3	II		2	95% EtOH	283	4.29	244	2.83
					320 ^a	3.60		
4	II		2	KOH-EtOH	310	4.53	264	3.10
					340 ^a	3.80		
10	III		2	95% EtOH	272	3.96	242	3.40
					348	3.45	302	2.91
9	IV		3	95% EtOH	253	3.88	237	3.62
					316	3.47	284	2.92
7	V		4	95% EtOH	238	4.20	286	3.61
					252 ^a	3.84		
					311	3.81		
8	VI		2	95% EtOH	247	4.19	233	4.06
					272	4.00	261	3.97
					345	3.43	315	3.24
1	VII		2	95% EtOH	250	4.03	230	3.92
2	VII		2	KOH-EtOH	278 ^a	3.98	270	3.96
					355	3.55	320	3.27
					413	3.51		
14	VIII		5	95% EtOH	238	4.05	345	1.86
					260 ^a	4.00		
					360	1.88		
13	VIII		5	KOH-EtOH	244	4.08		
					270 ^a	3.48		
15	IX		5	95% EtOH	296	3.11	278	3.07
					370 ^a	2.06		
11	X		6	95% EtOH	271	3.92	242	3.16
					344	3.36	302	2.84

(3) Cramer, Schroeder, Moran, Nield, Edwards, Jarowski and Puetzer, *J. Amer. Pharm. Assn. Sci. Ed.*, **37**, 439 (1948).(4) Ruhemann and Bausor, *J. Chem. Soc.*, **79**, 472 (1901).(5) Kozniowski and Marchlewski, *Bull. Acad. Sci. Cracow*, 81-95, (1906); *J. Chem. Soc. Abs.*, **90**, 1, 759 (1906).(6) Russell and Frye, "Organic Syntheses," **21**, 22 (1941).

TABLE I (Continued)

Curve Number	Structure of compound	Ref.	Solvent	λ_{\max} .	Log	λ_{\min} .	Log ϵ
12 XI		7	95% EtOH	276 340*	3.07 1.80	249	2.95

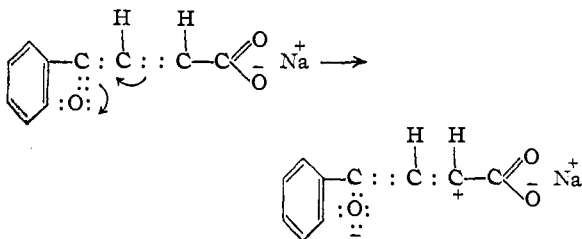
* Shoulder in curve.

The maxima and minima together with their log ϵ values for each curve are summarized in Table I.

In the absorption curves of simple α,β -unsaturated ketones the ethylenic band occurs between 220–250 $m\mu$.⁸ Although the compounds dealt with in this paper are not simple unsaturated ketones it is of interest to note that with the exception of the two trimethylphenyl derivatives (IX, XI), the ketonic compounds studied which are α,β -unsaturated (V, VI, VII and VIII) show a peak in the ethylenic region. In the curves for the substituted γ -chromanones (I, II, III, and IV) and 2,6-dihydroxyacetophenone there is no peak in the 220–250 $m\mu$ region. Consequently the absorption in this region appears to be significant in enabling one to choose between a β -aroyl acrylic acid and 2-carboxy- γ -chromanone structure.

A chromophoric relationship between *o*-hydroxyacetophenone and flavanones has been described by Tasaki.⁹ He showed that 2-hydroxyhydrochalcone gave a similar spectrum to flavanone. Notice the close agreement in the absorption curves of I and X. The curves for II and phloracetophenone are similarly related.¹⁰ These interrelationships are additional arguments in favor of the γ -chromanone structure for I and II.

The general effect of alkali on the absorption curves of the four examples shown is to cause a shift toward higher wave length. In the curve for compound VIII the carbonyl peak at 358 $m\mu$ is missing in alkaline solution. This suggests that in alkaline media the following might occur



The carboxylate ion, an electron-furnishing group, would favor a drift of electrons from the α -carbon to the carbonyl oxygen. Experimental evidence for the significant contribution made by such a resonance hybrid, in which the carbonyl oxygen has $-O^-$ character, is the easy addition of meth-

(7) Fuson and McKeever, *THIS JOURNAL*, **62**, 2088 (1940).

(8) Dimroth, *Angew. Chem.*, **52**, 553 (1939).

(9) Tasaki, *Acta Phytochim.*, **3**, 259 (1927).

(10) Russell, Todd and Wilson, *J. Chem. Soc.*, 1940 (1934).

anol to β -(*p*-bromobenzoyl)-acrylic acid in the presence of sodium methoxide.¹¹

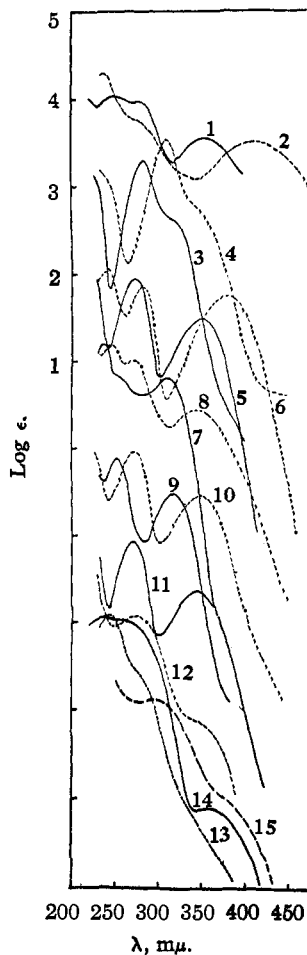


Fig. 1.

In the presence of alkali the λ_{\max} of I are shifted towards longer wave lengths. The new band at 243 $m\mu$ is most likely due to an opening of the γ -chromanone ring. It corresponds to the maximum at 238 $m\mu$ for VII and 244 $m\mu$ for VIII in alcoholic alkali. Thus it would appear that the chalcone- γ -chromanone type of equilibrium takes place with compound I and the failure to isolate β -(2,6-dihydroxybenzoyl)-acrylic acid is possibly a result of an easy cyclization of the latter upon acidification.

(11) Lutz and Scott, *J. Org. Chem.*, **18**, 284 (1948).

In order to ascertain the effect of alkali under more vigorous conditions, I was heated under reflux with 0.05 *N* alcoholic potassium hydroxide for thirty minutes. The solution was cooled to room temperature and the absorption spectrum determined. The curve is not shown since it was almost identical to that given for I after treatment with alkali at room temperature (Curve 6). The values found were: λ_{\max} , 241 $m\mu$ ($\log \epsilon = 4.01$), 285 $m\mu$ ($\log \epsilon = 3.89$) and 377 $m\mu$ ($\log \epsilon = 3.76$); λ_{\min} , 260 $m\mu$ ($\log \epsilon = 3.36$) and 309 $m\mu$ ($\log \epsilon = 2.75$).

Inspection of the absorption curve of compound II in alkali reveals the absence of a peak in the

220–250 $m\mu$ region. This would indicate a failure to open the γ -chromanone ring.

Summary

Studies on the ultraviolet absorption of some substituted β -benzoylacrylic acids, 2-carboxy- γ -chromones, and 2-carboxy- γ -chromanones have shown the significance of the maximum in the 220–250 $m\mu$ range which is present in the first two classes of compounds and missing in the third. The effect of alkali on the absorption curve and the use of such data for detecting the opening of the γ -chromanone ring has been pointed out.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEPARTMENT OF PHYSICS OF THE UNIVERSITY OF CHICAGO]

Geometry and Spectra of Substituted Anilines¹

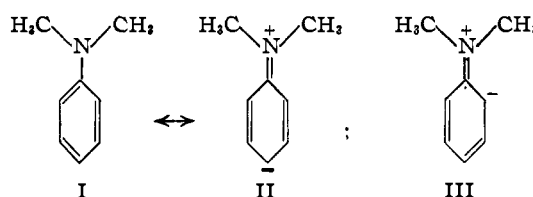
BY H. B. KLEVENS² AND J. R. PLATT

Steric inhibition of resonance effects on near ultraviolet absorption spectra have been investigated by numerous groups.³ Steric inhibition to planarity in dye molecules and its effect on their spectra in the visible region has been reviewed recently.⁴ The compounds reported here were studied by Remington⁵ in the 2200–3000 Å. region and a correlation of spectral characteristics and parallel chemical effects of steric inhibition of resonance was included. He indicated that the absorption band nearest the red was the one most affected by steric hindrance. The absorption curves for *N,N*-dimethylaniline and six of its derivatives have been extended to 1700 Å.

The observed chemical and spectroscopic effects of steric hindrance in conjugated systems may be interpreted as follows. As indicated by Pauling,⁵ resonance in conjugated systems implies approximate planarity of all the conjugated atoms, with the unsaturation electron orbitals oriented normal to the plane. Destruction of planarity by a "crowding" substituent causes one or more double-bond linkages to twist, losing part of their double bond character and partly destroying the conjugation. With 90° twist, a twisted link takes on some of the properties of a

single bond, insulating from each other the sections (which may still be locally planar and conjugated) on each side of it. In this case, the spectral absorptions of these two sections become approximately independent and additive, usually making a great change from the spectrum of the initial completely planar conjugated system. It is shown here that for intermediate angles of twist, the changes in the spectrum are quantitatively related to the angle of twist.

The *N,N*-dimethylaniline is supposed to be a resonance hybrid of structures I, II and III with the $-N(CH_3)_2$ group oriented so that the two methyl C-atoms are in or nearly in the plane of the ring. This orientation is favored because



it allows the formation of structures like II and III in which the N electrons can be partially conjugated with the unsaturation electrons of the ring. The ultraviolet spectrum is therefore not like that of toluene or of isopropyl or *s*-butylbenzene,⁶ where the alkyl substituent has no unsaturation electrons, but rather resembles that of styrene and diphenyl⁷ where there is full conjugation with the ring.

In the *N,N*-dimethylanilines it is the $-N(CH_3)_2$ group which twists with relation to the ring as groups of progressively larger radii are added in the ortho position. The twist causes progressive

(1) Presented before the Division of Physical and Inorganic Chemistry at the 113th meeting of the American Chemical Society at Chicago, Illinois, April 19–23, 1948.

(2) Present address: Division of Agricultural Biochemistry, University of Minnesota, St. Paul, Minnesota.

(3) For example see: Ley and Pfeiffer, *Ber.*, **54**, 363 (1921); Pickett, Walter and France, *THIS JOURNAL*, **58**, 2296 (1936); Thielacker and Ozegowski, *Ber.*, **73**, 898 (1940); O'Shaughnessy and Rodebush, *THIS JOURNAL*, **62**, 2906 (1940); Williamson and Rodebush, *ibid.*, **63**, 3018 (1941); Sherwood and Calvin, *ibid.*, **64**, 1350 (1942); Jones, *ibid.*, **65**, 1815, 1818 (1943); **67**, 2127 (1945); Remington, *ibid.*, **67**, 1838 (1945).

(4) Brooker, White, Sprague, Dent and Van Zandt, *Chem. Rev.*, **41**, 325 (1947).

(5) Pauling, "The Nature of the Chemical Bond," Chap. VI, Cornell University Press, Ithaca, New York, 2nd edition, 1944.

(6) J. R. Platt and H. B. Klevens, *Chem. Rev.*, **41**, 301 (1947); *J. Chem. Phys.*, **16**, 832 (1948).

(7) Unpublished results of the authors.