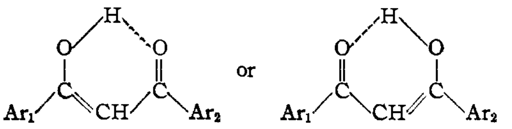
[CONTRIBUTION FROM HOWARD UNIVERSITY]

The Absorption Spectra of Some Enols and Related Intermediates[1]

By Lloyd N. Ferguson adn R. Percy Barnes

A 1,3-diketone, Ar$_1$-CO-CH$_2$-CO-Ar$_2$, may enolize in either one of two directions to give two isomeric enols with structures



A number of investigators[2] have used chemical means to determine this direction of enolization, but because the two isomeric enols are in equilibrium with each other through the common diketone it is very likely that what has been measured, in effect, is the relative rate of reaction of the isomeric enols in proportion to their concentrations at equilibrium. If one assumes, however, that the reaction rate constants for the two enols are nearly equal, then this view will not subtract from the reported results.

On the other hand, neither have physical studies[3] given very conclusive results as to the structure of the existing enolic modification of a 1,3-diketone. Following-up these physical studies, the spectra of several 1,3-diketones and related intermediates were measured to seek some correlation between the spectrum of an enol, Ar$_1$-CO-CH=C(OH)-Ar$_2$, with that of the corresponding methyl ether, Ar$_1$-CO-CH=C(OCH$_3$)-Ar$_2$, or with the chalcone, Ar$_1$-CO-CH=CH-Ar$_2$, which could be used as evidence for the structure of the enol. The wave length of the maximum absorption bands and the corresponding molecular extinction coefficients for the compounds studied are listed in Table I.

TABLE I

ULTRAVIOLET SPECTRAL CHARACTERISTICS OF SOME ENOLS AND RELATED INTERMEDIATES

	Compound	$\lambda_{max.}$, mμ	$\epsilon_{max.}$	$\lambda'_{max.}$, (mμ)	$\epsilon'_{max.}$
1	*p*-CH$_3$O—C$_6$H$_4$—CO—CH=CH—Mes[a]	319	24,000		
2	*p*-CH$_3$O—C$_6$H$_4$—C(OH)=CH—CO—Mes	332	28,550		
3	*p*-CH$_3$O—C$_6$H$_4$—CH=CH—CO—Mes	330	27,600	238	9,380
4	*p*-C$_2$H$_5$O—C$_6$H$_4$—CO—CH=CH—C$_6$H$_4$—OCH$_3$-*p*[b]	347	29,200	235	15,000
5	*p*-CH$_3$O—C$_6$H$_4$—CO—CH=CH—C$_6$H$_4$—OC$_2$H$_5$-*p*[b]	347	31,100	235	14,400
6	*p*-CH$_3$O—C$_6$H$_4$—CO—CH$_2$—CO—C$_6$H$_4$—OC$_2$H$_5$-*p*	364.5	42,750	293	10,540
7	*o*-O$_2$N—C$_6$H$_4$—C(OCH$_3$)=CH—CO—Mes[c]	263	18,700		
8	*o*-O$_2$N—C$_6$H$_4$—CO—CH=C(OCH$_3$)—Mes[c]	262	18,640		
9	*o*-O$_2$N—C$_6$H$_4$—C(OH)=CH—CO—Mes	305	13,160		
10	*o*-O$_2$N—C$_6$H$_4$—CO—CH=CH—Mes	310	15,200		
11	*o*-O$_2$N—C$_6$H$_4$—CH=CH—CO—Mes	252	18,900		
12	*p*-Br—C$_6$H$_4$—CO—CH=CH—C$_6$H$_4$—OCH$_3$-*p*	348.5	19,500	265	15,370
13	*p*-CH$_3$O—C$_6$H$_4$—CO—CH=CH—C$_6$H$_4$—Br-*p*	322	26,950	230.5	15,470
14	*p*-CH$_3$O—C$_6$H$_4$—CO—CH$_2$—CO—C$_6$H$_4$—Br-*p*	358	35,400	215	10,790
15	*m*-O$_2$N—C$_6$H$_4$—CH=CH—CO—Mes	278	28,050		
16	*m*-O$_2$N—C$_6$H$_4$—CO—CH=C(OH)—Mes	324	6,000		
17	Mes-C(OCH$_3$)=CH—CO—C$_6$H$_4$—OCH$_3$)-*p* (m. p. 102°)	298.5	25,700		
18	Mes-C(OCH$_3$)=CH—CO—C$_6$H$_4$—OCH$_3$-*p* (m. p. 91°)	330	31,300	237	20,040

[a] Mes is used throughout this article to represent the mesityl group. [b,c] The spectra of these compounds may be almost superimposed upon one another.

TABLE II

WAVE-LENGTH OF THE MAXIMUM ABSORPTION BAND OF SOME CHALCONES

Compound	$\lambda_{max.}$, mμ	Shift, mμ
C$_6$H$_5$—CH=CH—CO—C$_6$H$_5$	(313)[a,b,c]	
o-O$_2$N—C$_6$H$_4$—CO—CH=CH—Mes	310	− 3
o-O$_2$N—C$_6$H$_4$—CH=CH—CO—Mes	252	−61
p-CH$_3$O—C$_6$H$_4$—CO—CH=CH—Mes	319	+ 6
p-CH$_3$O—C$_6$H$_4$—CH=CH—CO—Mes	330	+17
p-CH$_3$O—C$_6$H$_4$—CH=CH—CO—C$_6$H$_4$—Br-*p*	348.5	+35.5
p-CH$_3$O—C$_6$H$_4$—CO—CH=CH—C$_6$H$_4$—Br-*p*	322	+ 9
p-CH$_3$O—C$_6$H$_4$—CO—CH=CH—C$_6$H$_4$—OC$_2$H$_5$-*p*	347	+34
p-CH$_3$O—C$_6$H$_4$—CH=CH—CO—C$_6$H$_4$—OC$_2$H$_5$-*p*	347	+34
m-O$_2$N—C$_6$H$_4$—CH=CH—CO—Mes	278	−35

[a] D. Rădulescu, *Ber.*, 64, 2243 (1931). [b] A. Russell, J. Todd and C. L. Wilson, *J. Chem. Soc.*, 1940 (1934). [c] V. Alexa, *loc. cit.*

From the results it is found that little can be stated concerning the structure of the enolic modification of a 1,3-diketone on the basis of its spec-

---

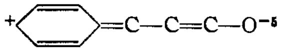
(1) Presented before the organic division of the Washington Chemical Society, October, 1947.

(2) Notably, Barnes and co-workers, THIS JOURNAL, **69**, 3135 (1947), and earlier papers, and Shenoe, Shah and Wheeler, *J. Chem. Soc.*, 247 (1940).

(3) Smedley, *J. Chem. Soc.*, **97**, 1484 (1910); Morton, Hassan and Calloway, *J. Chem. Soc.*, 883 (1934); Lowry, *et al.*, *J. Chem. Soc.*, 1333, 3167 (1928); Sugden, *J. Chem. Soc.*, 316 (1929).

trum and the spectra of related enol-ethers and chalcones. Nevertheless, it is observed[4] that (1) the isomeric enol-ethers can have almost identical spectra (compounds 3 and 4), (2) the *cis* and *trans* forms of an enol-ether have very different spectra (compounds 17 and 18), (3) the $\lambda_{\max.}$ of an enol-ether is quite different from that of the enol or the related chalcone, and (4) the diketones containing substituents in the ortho positions of the phenyl ring have $\lambda_{\max.}$ less than 335 mμ and of relatively low intensity (compounds 2, 9 and 16).

It may be assumed that the main chromophoric system in the chalcones is C_6H_5–C=C–C=O, probably due to the resonant form



Thus, any group attached to the phenyl ring which readily accepts the positive charge, such as an alkoxyl group, will have a bathochromic effect while negative groups (NO_2, COOH, etc.) will have the opposite effect. Non-resonating groups, such as the methyl group, will have only a small influence on $\lambda_{\max.}$. These expectations are found to be true, in general, upon inspection of the $\lambda_{\max.}$ listed in Table II.[6] The third column gives the difference from the $\lambda_{\max.}$ of the unsubstituted benzalacetophenone.

Experimental

The absorption measurements were made using a Beckman Photoelectric Quartz Spectrophotometer, Model DU, with 1-cm. square, fused silica, absorption cells. Ninety-five per cent. ethanol served as the solvent. All of the compounds were prepared by students and their analyses agreed with the calculated values.

Summary

The spectra of several 1,3-diketones, Ar_1–CO–CH_2–CO–Ar_2, and of related enol-ethers, Ar_1–CO–CH=C(OCH_3)–Ar_2, and chalcones, Ar_1–CO–CH=CH–Ar_2, have been measured and the wave length, $\lambda_{\max.}$, of their maximum absorption bands are herein reported. Several observations are made and discussed regarding the $\lambda_{\max.}$ of the enol-ethers and of chalcones containing very different groups Ar_1 and Ar_2.

WASHINGTON, D. C. RECEIVED APRIL 30, 1948

---

(4) The authors are indebted to an unknown referee for a part of the view-point presented here.

(5) Compare discussion by Katzenellenbogen and Branch, THIS JOURNAL, **69**, 1615 (1947).

(6) Additional examples may be found among the spectra reported by Alexa for a large number of substituted chalcones, V. Alexa, *Bul. Chim., Soc. Chim. România*, [2] **1**, 77 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Synthesis and Investigation of Pyridine and Pyrazine Analogs of Salicylates[1,2]

BY LEWIS R. FIBEL[3] AND PAUL E. SPOERRI

The pyridine hydroxycarboxylic acids, as contrasted with their benzene analogs, are not adequately described in the literature. Some of them were therefore synthesized and their properties investigated.

As representative of heterocyclic analogs of salicylic acid, we have prepared 2-hydroxynicotinic acid, 3-hydroxypicolinic acid, chelidamic acid (4-hydroxypyridine-2,6-dicarboxylic acid) and 3-hydroxypyrazinoic acid. We also synthesized 2-mercaptonicotinic acid, analogous to thiosalicylic acid.

Tautomerism of the hydroxyl group would lead to a carbonyl configuration, as has been shown in 2-hydroxypyridine–α-pyridone. Standard procedures were applied to 2-hydroxynicotinic acid in attempts to produce the oxime, phenylhydrazone, *p*-nitrophenylhydrazone, and 2,4-dinitrophenylhydrazone, but all the attempts were unsuccessful. Analogous heterocyclic carbonyl groups directly attached to the ring rarely form oximes or hydrazones.[4]

3-Aminopicolinic acid has been prepared by the Hofmann degradation of quinolinic imide or amide. Sucharda[5] used the action of sodium hypochlorite on the imide. Ochiai and Arai[6] used hypobromous acid on the imide, and Kirpal,[7] sodium hypobromite on quinolinic acid α-amide. We obtained best results using sodium hypobromite on the imide.

From chelidamic acid, we prepared dimethyl chelidamate by the usual esterification procedure using methanol and sulfuric acid. It was obtained as the monohydrate and, on saponification, chelidamic acid was regenerated. Meyer[8] prepared what he claimed to be dimethyl chelidamate by the action of diazomethane on chelidamic acid.

By the action of diazomethane on chelidamic

---

[1] Presented in part at the meeting of the American Chemical Society, New York, September 15–19, 1947.

[2] Abstracted from the dissertation presented to the Graduate Faculty by Lewis R. Fibel in partial fulfilment of the requirements for the Ph.D. degree, June, 1947.

[3] Present address: W. M. Grosvenor Laboratories, Inc., 50 East 41st Street, New York, N. Y.

(4) Exceptions are noted by Petrenko-Kritschenko and Mosseschwili, *J. prakt. Chem.*, [2] **64**, 496 (1901); Bedekar, Kaushal and Deshapande, *J. Indian Chem. Soc.*, **12**, 465 (1935); and Cawley and Plant, *J. Chem. Soc.*, 1214 (1938).

(5) Sucharda, *Ber.*, **58**, 1727 (1925).

(6) Ochiai and Arai, *J. Pharm. Soc. Japan*, **59**, 458 (1939); *C. A.*, **34**, 108 (1940).

(7) Kirpal, *Monatsh.*, **29**, 228 (1908).

(8) H. Meyer, *ibid.*, **26**, 1311 (1905); **25**, 1193 (1904).