

THE BECKMANN REARRANGEMENT. VI. THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME AROMATIC OXIMES

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In the preceding paper (1) the unusually fast rates of rearrangement of *ortho*-substituted acetophenone oximes were attributed primarily to the prevention of co-planarity between the aromatic ring and the α -oximinoethyl grouping ($=C=NOHCH_3$) by the *ortho* substituent. Physical evidence was sought to substantiate this view, and the work of Hedden and Brown (2) provided a good foundation for obtaining physical evidence. They pointed out that the most characteristic absorption band of aromatic ketones occurred in the region of about 240 $m\mu$ and that this conjugation band, called the C band, most clearly reflected the geometrical relationship between the phenyl and carbonyl groups. They found that the effect of two *ortho* substituents was a marked diminution in the intensity of the C band and that the effect of one *ortho* substituent was a slight diminution overshadowed by the electrical influence of the group.

With this background the absorption spectra of a number of aromatic oximes were studied both in isoöctane as a solvent and in concentrated sulfuric acid. The results are recorded in Table I. Sulfuric acid seemed the more appropriate solvent since it was the medium for rearrangement. It proved also to be much the better solvent for comparison of spectra. The absorption maxima for all oximes were not only shifted to longer wavelengths but they were also further separated—for example, the C band for most oximes occurred between 243–252 $m\mu$ in isoöctane and between 270–298 $m\mu$ in sulfuric acid.² Most of the comments, therefore, refer to the absorption spectra in concentrated sulfuric acid in which the oxime is probably in the form of an oxonium or immonium salt.

The spectra of the acetophenone oximes substituted in the *meta* and *para* positions apparently are perfectly normal (Table I). *p*-Nitro, *p*-halo and *p*-methoxy groups which conjugate with the benzene ring produce a pronounced shift of the maximum of the C band toward longer wavelength. The shift occurs whether the group is electron-withdrawing or -releasing, suggesting that conjugation is the predominant influence in any shift of the C band. The one exception in this series is the *m*-nitro group which leads to a shift toward shorter wavelength probably because of cross-conjugation. The intense absorption of this compound is probably the result of the additivity of the two at least partly independent conjugated systems both of which absorb at the same wavelength. The *m*- and *p*-alkyl groups which are capable of electron release by induction also shift the C band toward longer wavelength (Table I; see also examples in

¹ Taken from part of the Ph.D. thesis of Exum D. Watts, Vanderbilt University, 1954.

² Sweeney and Schubert (11) have observed similar effects with ketones in concentrated sulfuric acid.

TABLE I
 ULTRAVIOLET ADSORPTION SPECTRA OF AROMATIC OXIMES

Acetophenone oxime	In Isooctane		In Sulfuric Acid		Bathochromic Shift ^j	
	Max. (m μ)	$\epsilon \times 10^{-3}$	Max. (m μ)	$\epsilon \times 10^{-3}$	<i>ortho</i> or <i>meta</i>	<i>para</i>
2-Methyl	228	6.84	272 ^d	4.17	2	
3-Methyl	245	11.23	275	12.67	5	
4-Methyl	249	15.12	288	14.77		18
3,5-Dimethyl	249	11.36	283	12.74		
2,4-Dimethyl	235	8.70	255	11.94	-15	
3,4,5-Trimethyl	252	13.34	298	15.01		28
4- <i>tert</i> -Butyl	248	15.59	290	17.14		20
Unsubstituted	243	11.58	270	13.22		
2-Chloro	End absorption		268	6.89	-2	
4-Chloro	250	17.04	283 ^e	16.79		13
4-Bromo	254	18.89	290 ^f	17.49		20
4-Iodo	261	24.15	308 ^g	16.40		38
2-Nitro	265	7.42 ^a	279	6.60	9	
3-Nitro	242	26.40 ^a	251	22.39	-19	
4-Nitro	†		In visible range. ^h			Large
2-Methoxy	234 ^c	9.10				
4-Methoxy	257	15.65	297 ⁱ	15.46		27
Pivalophenone oxime	End absorption					
4-Methyl	277	4.32				
4-Bromo	275	3.77 ^a				

^a Minimum value because of poor solubility in isooctane. ^b B band (2): 283 m μ , 10.88 $\times 10^3$. Other B bands in m μ and $\epsilon \times 10^{-3}$ are given in *c* through *i*. ^c 282, 2.88. [The B and C bands of the 2-methoxy oxime may be reversed; the selection in this Table was based on the fact that the B band of anisole in heptane is at 282 m μ (10).] ^d 248, 6.73 ^e 220, 8.69 ^f 222 8.40 ^g 230, 7.67 ^h 278, 16.96 ⁱ 224, 7.98 ^j Difference in wavelengths between substituted and unsubstituted acetophenone oximes; the left column shows small or no bathochromic shift; the right column shows much greater effect of substituents in *para* position.

Fig. 1). In fact, as suggested by similar infrared studies (3), the shift by the inductive mechanism can be roughly correlated with Hammett's *sigma* constants as shown in Fig. 2. The correlation would be better if the *m*-methyl *sigma* constant were less negative or if the *p*-methyl constant were more negative.³ The *para*-alkyl groups not only shift the C band toward longer wavelength but also intensify the absorption. The *meta*-methyl group has little effect on the intensification.

³ It is difficult to decide which of two explanations leads to discrepancies found in Fig. 2. The first explanation may be that the *m*-methyl *sigma* constant (-0.069) is uncertain (4) and should be less negative. This explanation does not seem reasonable since a value of even greater negativity (-0.10) has been proposed (5) and used for other work (6). The second explanation may be that the *p*-methyl *sigma* constant (-0.17) is more negative when its influence on the C band shift is assessed. This explanation suggests a hyperconjugative influence, which must also be extended to explain the influence of the *tert*-butyl group, as shown in Fig. 2. A hyperconjugative influence of the *tert*-butyl group of the same order of magnitude as the *p*-methyl group hardly seems likely.

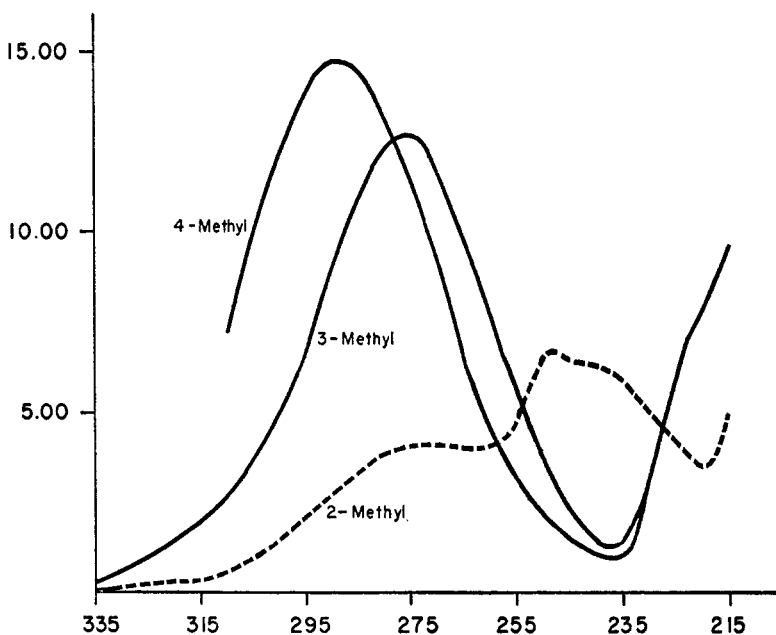


FIG. 1. ULTRAVIOLET ABSORPTION CURVES OF METHYL-SUBSTITUTED ACETOPHENONE OXIMES IN 94.5% SULFURIC ACID. Extinction coefficient $\times 10^{-3}$ versus wave-length in $m\mu$.

The spectra of the *ortho*-substituted acetophenone oximes are completely different from the spectra of their isomers. The differences are illustrated for the methyl-substituted oximes in Fig. 1 and can be noted for the other series in Table I. In all of the *ortho*-substituted oximes, the intensification is drastically reduced and the shift of the C band toward longer wavelength is practically *nil*. The spectral differences of the *ortho*-substituted oximes from their isomers are much greater than those that Hedden and Brown (2) found for the *ortho*-substituted ketones. The explanation is probably that the bulkier α -oximinoethyl grouping is twisted further out of the plane of the ring system than is the aceto grouping.

The study of the ultraviolet spectra of aromatic oximes therefore supports the view that coplanarity between the benzene ring and the α -oximinoethyl grouping has been reduced by the *ortho* substituent.

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EXPERIMENTAL

The oximes were available from previous work (1, 6, 7) with the following exceptions: *4*-iodoacetophenone oxime, m.p. 162.5–163.5°; *4*-bromoacetophenone oxime, m.p. 129–130°; *2,4*-dimethylacetophenone oxime, m.p. 65.5–67°. The oximes were each recrystallized a number of times from ethanol. Solutions for spectral determinations were made from 5.5×10^{-4} mole of oxime in 100 ml. of solvent—1 ml. of this solution being diluted further to 100 ml. The solvents were "spectro" grade isoöctane, Phillips Petroleum Co., and sulfuric

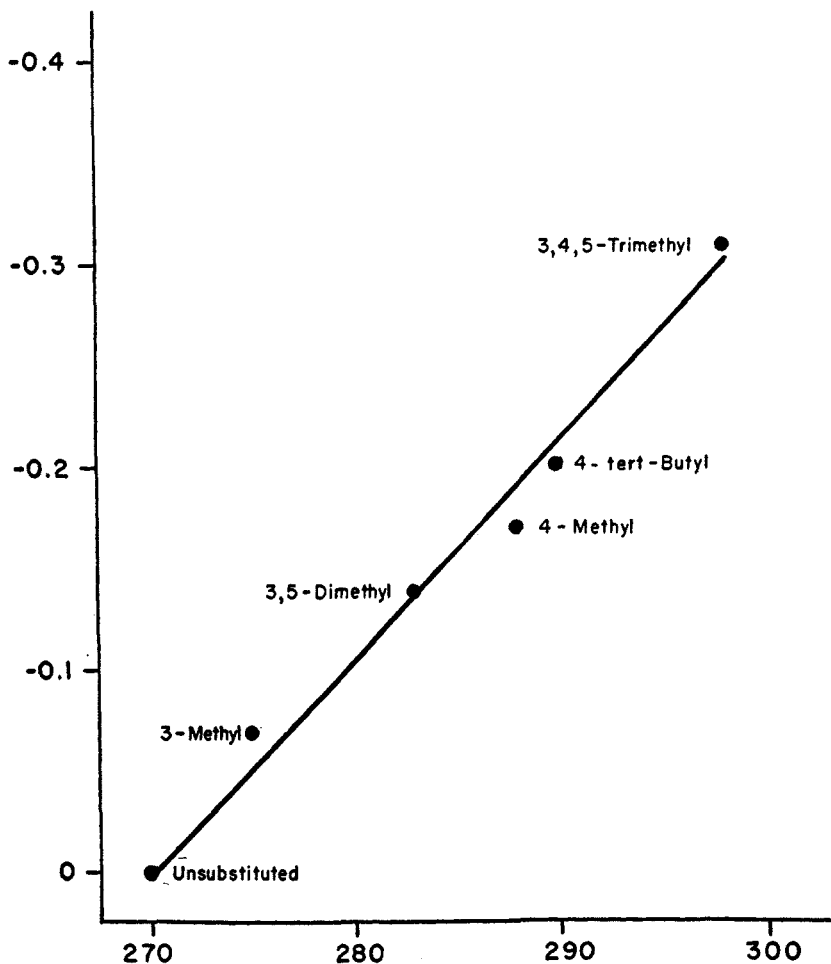


FIG. 2. HAMMETT σ CONSTANTS versus WAVELENGTH (in $m\mu$) OF MAXIMUM ABSORPTION FOR ALKYL-SUBSTITUTED ACETOPHENONE OXIMES DISSOLVED IN 94.5% SULFURIC ACID.

acid, 94.5%, Merck Co. Determinations in the latter solvent were made as rapidly as possible to minimize interferences from rearrangement products. Negligible rearrangement is to be expected under these conditions with all oximes with the possible exception of 2-methyl- and 2,4-dimethyl-acetophenone oximes. Determinations were made with the Beckman Spectrophotometer, Model DU, newly calibrated against the hydrogen line at 656.3 $m\mu$.

The absorption maximum of acetophenone oxime has been reported to be at approximately 244 $m\mu$ compared with the value in this paper of 243 $m\mu$ (8). 2-Chloroacetophenone oxime (8) and pivalophenone oxime (9) are reported to have end absorption in accord with the results of this paper.

SUMMARY

The absorption spectra of *ortho*-substituted acetophenone oximes are completely different from those of the corresponding *meta*- and *para*-oximes. The

explanation is believed to be the reduction of coplanarity between the α -oximinoethyl grouping and aromatic ring system.

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