[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

α,β-Unsaturated Aminoketones. IX.[1] Color and Constitution

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The absorption of light by organic substances in the visible and near ultraviolet ranges of the spectrum is undoubtedly associated with the resonance phenomenon in systems that contain multiple bonds. The introduction of so-called auxochromic groups into such systems causes a shift of the absorption toward the red, only when such a modification is in such a position as to cause resonance to be enhanced.[2]

The introduction into a system of multiple bonds of a group that can carry the charge better than carbon may be done in two different ways. If the substitution is in such a position as to enhance the resonance of a given group of oscillators by contributing to their degeneracy without increasing the length or altering the general nature of such oscillators extensively, then only the extinction coefficient of absorption will be increased without necessarily causing a large shift in the position of the maxima. However, if the introduction of such auxochromic groups is in some other possible position in the conjugated systems, such as to change the nature or length of possible resonance oscillators, then one may expect a substantial shift in the position of the maxima.

The present communication reports the study of the absorption spectra of certain unsaturated amino ketones and of ethylene imino ketones that have been prepared in other investigations in this series.

It had been observed that the presence of a secondary amino group in the α-position of an α,β-unsaturated ketone always produced considerable visible color in the solid substances. Likewise, it was seen that the presence of these same groups in the β-position of these molecules developed no appreciable visible color in the solid substances. Furthermore, it had been noted that the so-called α-aminobenzalacetophenone which has been prepared by several investigators[3] was not deeply colored. In paper VIII[1] in this series it has been shown that the reactions of primary amines with bromine derivatives of benzalacetophenone also lead to colorless substances in contradistinction to the colored products obtained by the use of secondary amines in these same reactions. It seemed important to compare and contrast the absorption spectra of these various substances.

It was observed that the presence of a secondary amino group in the α-position of the benzalacetophenone molecule gave solutions in absolute alcohol which showed rather general absorption in the region of 3500 to 4100 Å. with the heads of the bands close to 4000 Å., and extinction coefficients of the order of 2×10^{-3} to 3×10^{-3} (see table). In benzene solution the maxima of these substances were shifted slightly in some cases toward the ultraviolet and the extinction coefficients were increased somewhat.[4]

As had been expected, the presence of such secondary amino groups in the β-position of these conjugated unsaturated systems had little effect on the position of the maxima but did cause a marked increase in the extinction coefficients of these substances ($\epsilon_{\max}$ varied from 20×10^{-3} to 14×10^{-3} at $\lambda = 3500$ Å. in alcohol solutions) over that of the parent benzalacetophenone ($\epsilon_{\max} = 2.04 \times 10^{-3}$ at $\lambda = 3350$ Å. in alcohol solution). In benzene solutions the spectra of the β-amino-α,β-unsaturated ketones showed maxima at slightly shorter wave lengths and lower extinction coefficients.

The presence of a bromine atom in the α-position of benzalacetophenone gave little change in the position of the maximum but decreased the extinction coefficient considerably ($\epsilon_{\max} = 0.876 \times 10^{-3}$ at $\lambda = 3300$ Å. in alcohol solutions). However, the presence of a bromine atom in the α-position and an amino group in the β-position greatly increased the value of $\epsilon_{\max}$ and shifted $\lambda_{\max}$ considerably toward the red. ($\epsilon_{\max} = 18.5 \times 10^{-3}$ at $\lambda = 4025$ Å. in alcohol solution.)

Colorless substances which previous chemical investigations[1] have indicated as having ethylene imino ketone structures were found to show only a maximum (*i. e.*, 2-phenyl-3-benzoylethylenimine, $\epsilon_{\max} = 0.0430 \times 10^{-3}$ at $\lambda = 3250$ Å. in

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(1) For paper VIII in this series see Cromwell, Babson and Harris, THIS JOURNAL, **65**, 312 (1943).

(2) Bury, *ibid.*, **57**, 2115 (1935).

(3) Ruhemann and Watson, *J. Chem. Soc.*, **85**, 1181 (1904); Dufraisse and Moureu, *Bull. soc. chim.*, [4] **41**, 861 (1927); Blatt, THIS JOURNAL, **61**, 3494 (1939).

(4) Similar distortions have been noted for *p*-substitution products of benzalacetophenone by Alexa, *Bul. soc. chem. Romania*, **18A**, 67-101 (1936).

TABLE I

ABSORPTION MAXIMA OF AMINO KETONES

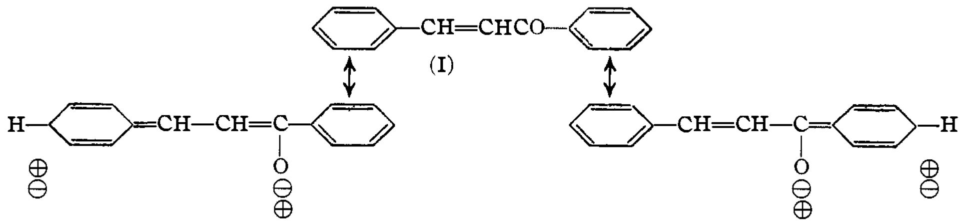
Ketone	M. p., °C.	Color solids	Max. abs. band in range from 3100–7000 Å. Abs. alcohol λ Å.	$\epsilon \times 10^{-3}$	Dry benzene λ Å.	$\epsilon \times 10^{-3}$
Benzylacetophenone	72	White	3275	0.0418	3275	0.0331
Benzalacetophenone	59	Pale yellow	3350	2.040	3275	1.468
2-Phenyl-3-benzoylethylenimine[a,b]	101	Pale yellow	3250	0.0430	3250	0.0465
1-Benzyl-2-phenyl-3-benzoylethylenimine[b]	108	White	3275	0.0623	3325	0.0686
1-Cyclohexyl-2-phenyl-3-benzoylethylenimine[b]	107	White	3300	0.0700	3350	0.0745
β-Morpholinobenzalacetophenone[c]	98	Pale yellow	3500	20.48	3450	16.98
β-N-Diethylaminobenzalacetophenone[d]	62	White	3500	18.50	3425	15.10
β-Benzylaminobenzalacetophenone[b]	101	Pale yellow	3450	14.58		
					3950	15.40
β-Piperidino-α-bromobenzalacetophenone[e]	142	Orange-yellow	4025	18.50	(λ min.)	(ε min.)
					3300	6.85
α-Morpholinobenzalacetophenone[c]	96	Orange	3700	3.265	3650	3.790
			4000	2.017	4000	2.820
α-N-Diethylaminobenzalacetophenone[d]	54	Orange-red	(λ min.)	(ε min.)	(λ min.)	(ε min.)
			3650	1.960	3625	2.683
α-Piperidinobenzalacetophenone[f]	102	Orange-red	3850	3.024		
			4100	2.040		
α-Pyrrolidinobenzalacetophenone[g]	98	Orange-red	(λ min.)	(ε min.)		
			3500	1.750		
			4000	2.552		
α-N-Methylbenzylaminobenzalacetophenone[h]	75	Orange-red	(λ min.)	(ε min.)		
			3500	1.960		
α-Bromobenzalacetophenone[c]	45	Pale yellow	3300	0.876	3300	0.667

These ketones were freshly prepared and recrystallized several times from the appropriate solvent for these experiments according to the methods given in the following: [a] Dufraisse and Moureu, *Bull. soc. chim.*, [4] **41**, 861 (1927). [b] Cromwell, *et al.*, THIS JOURNAL, **65**, 312 (1943). [c] *Ibid.*, **62**, 2897 (1940). [d] *Ibid.*, **62**, 1672 (1940). [e] Dufraisse, *et al.*, *Bull. soc. chim.*, [4] **51**, 550 (1932). [f] *Ibid.*, **41**, 457 (1927). [g] Cromwell, THIS JOURNAL, **63**, 2984 (1941). [h] Cromwell and Witt, *ibid.*, **65**, 308 (1943).

alcohol solution) of about the same nature as that of the parent saturated ketone (*i. e.*, benzylacetophenone, $\epsilon_{\max} = 0.0418 \times 10^{-3}$ at $\lambda = 3275$ Å. in alcohol solution). Dilute hydrochloric acid solutions of all of the amino ketones listed in the table were colorless.

The absorption spectra of these substances were studied over the entire range indicated at concentrations varying from 0.01 *M* for ethylene imines and benzylacetophenone to 0.0001 *M* for the β-amino-α,β-unsaturated ketones. Measurements of percentage transmission at intervals of 50 to 100 Å. were made with a Coleman Universal Spectrophotometer, using proper filters and operating at 10–11 volts over the entire range in wave length. Certain maxima, such as that for α-N-diethylaminobenzalacetophenone were checked with a Coleman Double-Monochromatic Spectrophotometer.

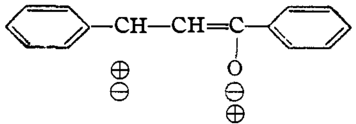
Discussion of Resonance and Structure.—Possible important resonance oscillators that may be written to approximate the true resonance hybrid of benzalacetophenone may be represented by the following extreme Lewis electron formulas.



(I)

(Ia) (Ib)

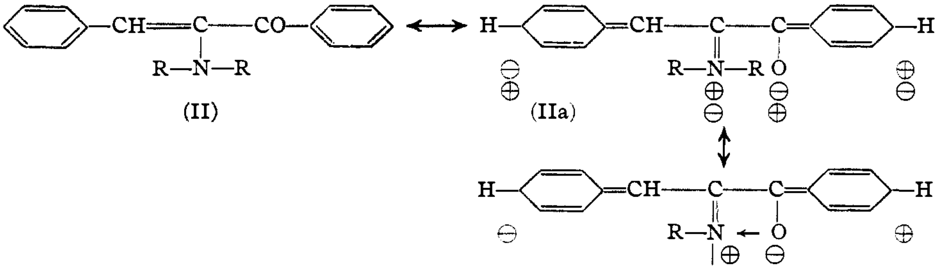
Resonance configurations (Ia) and (Ib) would not be expected to contribute much to the resonating system (Ia) ⟷ (I) ⟷ (Ib), since they both contain a quinoid structure. Possibly the Lewis electron structures



(Ic)

are of greater importance, although the degeneracy of any of these systems would be low. Thus benzalacetophenone shows only a small shift toward the red but considerable increase in ϵ_{max} as compared with the saturated ketone benzylacetophenone.

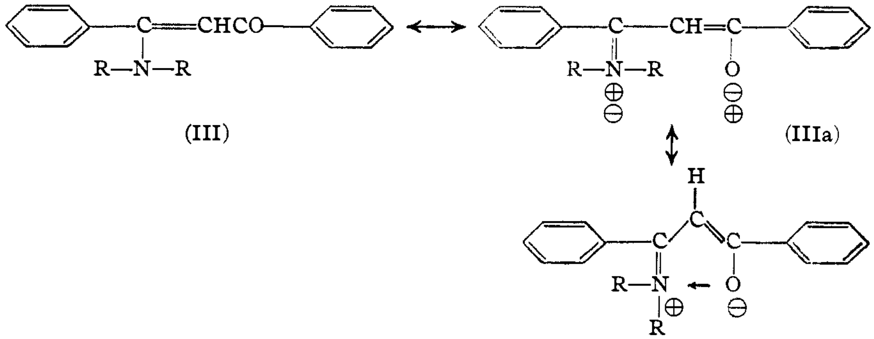
The introduction of secondary amino groups in the α-position of the benzalacetophenone molecule enhances the chance for resonance by allowing the development of new oscillators terminated by a nitrogen containing group, thus facilitating the movement of the charge through the molecule. It is of interest to consider the possibility of the relative importance of the following Lewis electron structures



(II) (IIa) (IIb)

Although the degeneracy of the system (II) ⟷ (IIa) ⟷ (IIb) might not be expected to be great because of the requirement of quinoid structures and a separation of charge, the tendency to form (IIb)[5] may be sufficient to overcome, somewhat, this other degeneracy-inhibiting effect. Certainly the nature of the oscillator in these substances varies considerably from that possible in the parent benzalacetophenone (I), and consequently a shift in the position of the maxima is to be expected, with or without a change in the magnitude of such maxima.

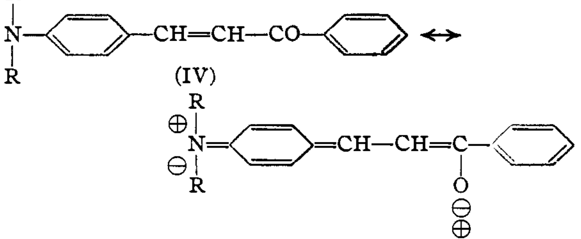
The introduction of such secondary amino groups into the β-position of benzalacetophenone would be expected to increase markedly the degeneracy of the resonance system (III) ⟷ (IIIa) ⟷ (IIIb)[5] as compared with the degeneracy of the similar system, (I) ⟷ (Ic). However, since the nature of the oscillator would not be greatly changed one might expect only a small shift in the position of the maxima but a considerable increase in the magnitude of ϵ_{max}.



(III) (IIIa) (IIIb)

It is not possible to indicate by Lewis electron structures variations of (III) which contain quinoid systems conjugated with a positively charged nitrogen atom.

It is interesting to note that according to Bogert,[6] ortho- and para-aminobenzalacetophenones are generally more deeply colored (*i. e.*, $\epsilon_{max} = 25.5 \times 10^{-3}$ at $\lambda = 3890$ Å.) than the corresponding meta isomers (*i. e.*, $\epsilon_{max} = 25.0 \times 10^{-3}$ at $\lambda = 3130$ Å.).



(IV) (IVa)

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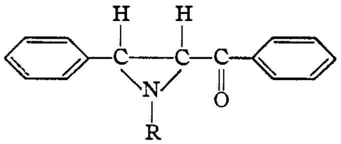
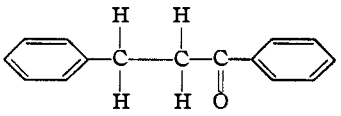
[5] By formulas (IIb) and (IIIb) we intend to imply only the means for maximum electron mobility throughout the oscillators.

[6] Price, Dingwall and Bogert, THIS JOURNAL, **56**, 2483 (1934).

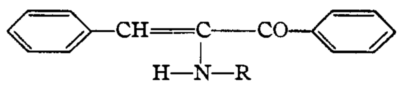
Here the importance of a Lewis electron structure containing a quinoid system is greatly enhanced by the presence of the terminal nitrogen containing group, and the degeneracy of the system (IV) ⟷ (IVa) would be expected to exceed that of (I) ⟷ (Ia). It will be interesting to study the spectra of α,β-unsaturated ketones containing amino groups on both the benzene rings and the aliphatic chain.

The ethylene imino ketones (V)[1] would not be expected to show color maxima that differed greatly from that of the parent saturated benzylacetophenone (VI).

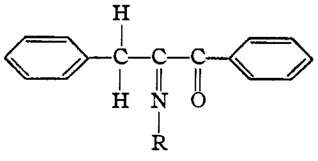

(V)


(VI)

However, had these substances actually had the structure (VII) assigned to them by previous investigators,[3] then they would have been expected to show absorption maxima similar to those observed for the α-secondary-amino-α,β-unsaturated ketones.


(VII)

Although it cannot be said with certainty that this study eliminates the possibility for still another alternative structure (VIII) for these substances this latter structure would be expected to show a greater value[1] for $\epsilon_{\max}$ even though the position of the maximum might not be expected to differ greatly from that of (VI).


(VIII)

An explanation of the relation between the absorption spectra and resonance of α-bromo-α,β-unsaturated ketones and α-bromo-β-amino-α,β-unsaturated ketones must await further experimentation.

No claim is made here for the exactness of these values for absorption maxima as determined by this method. However, these studies served to confirm the generalizations that seemed apparent from the appearance of these substances.

Complete absorption spectra studies for various unsaturated amino ketones and ethylene imino ketones in the benzalacetophenone and benzalacetone series are the subjects of further investigations in these Laboratories.

We appreciate very much a grant from the University Research Council which made this investigation possible.

Summary

1. α-Aminobenzalacetophenones have been shown to have an absorption maximum at approximately 4000 Å. while the β-amino isomers showed maxima at shorter wave lengths by approximately 500 Å. This difference has been attributed to a difference in the nature of the resonance oscillators of the substances.

2. Ethylene imino ketones, which do not have conjugated unsaturation as do the unsaturated amino ketones, show only a maximum similar to that observed for the parent saturated ketone, benzylacetophenone.

LINCOLN, NEBRASKA RECEIVED NOVEMBER 18, 1942