ULTRAVIOLET ABSORPTION SPECTRA OF SOME AMINO-SUBSTITUTED UNSATURATED KETONES

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In a previous investigation (1) the absorption spectra of some amino-substituted α,β-unsaturated ketones and related compounds were measured between 310 and 700 mμ. In that paper a general discussion of the resonance possibilities in such structures and their relationships to the spectra was given. At that time it was stated that a more complete study of the ultraviolet absorption spectra of such compounds was being undertaken. The earlier study included derivatives of only one α,β-unsaturated ketone, namely, benzalacetophenone. It was of interest to extend the study to derivatives of other α,β-unsaturated ketones such as benzalacetone and ethylideneacetophenone to observe the effect on the spectra of the presence and location of the phenyl groups.

The compounds (I)–(XV) for this investigation were freshly prepared, either according to methods given in the literature or as indicated in the experimental section. No one had previously reported the preparation of an α-amino derivative of ethylideneacetophenone. α-Bromoethylideneacetophenone was prepared for the first time from the dibromide of ethylideneacetophenone (2) by a modification of the method previously described for α-bromobenzalacetone (3). Morpholine was then added to the α-bromoethylideneacetophenone to give the crude α-bromo-β-morpholinobutyrophenone. This latter product was treated with sodium ethoxide, in the manner previously described for preparing α-aminobenzalacetones (4), to give α-morpholinoethylideneacetophenone (VIII).

β-Morpholinobenzalacetone (XI) was prepared from phenylacetylacetylene by a method similar to that described by Andre (5) for related compounds.

EXPERIMENTAL[1]

α-Bromoethylideneacetophenone. A 30.0 g. sample of α,β-dibromobutyrophenone (2), m.p. 95–97°, and 9.0 g. of sodium acetate were mixed with 75 ml. of 95% alcohol. This mixture was refluxed for four hours. The cooled reaction mixture was filtered to remove the sodium bromide, and the solvent removed under reduced pressure. The product was extracted from the residue with ether. The ether solution was washed several times with saturated saltwater and twice with saturated, aqueous sodium bicarbonate solution. The ether solution was dried and evaporated. The residual semi-solid product was recrystalized from 95% alcohol to give 15 g. of colorless crystals, m.p. 70–71°.

Anal. Calc'd for $C_{10}H_9BrO$: C, 53.33; H, 4.03; Br, 35.51.

Found: C, 53.41; H, 4.27; Br, 35.54.

α-Morpholinoethylideneacetophenone, (VIII). A 10.0 g. sample of α-bromoethylidene-acetophenone was dissolved in 30 ml. of a 50-50 dry ether-petroleum ether mixture. This solution was cooled to 0° and 5.0 g. of morpholine added. After standing in the ice-chest for twelve hours the waxy, precipitated material was removed, washed with water, dried

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[1] The micro analyses for carbon, hydrogen, nitrogen and bromine were determined by the Clark Microanalytical Laboratories of Urbana, Illinois.

and recrystallized from petroleum ether to give 5.0 g. of the crude addition product, m.p. 85–91°. This slightly yellow product was added to a boiling solution of 0.48 g. of sodium in 12 ml. of absolute alcohol. The reaction mixture was cooled and cold water added to precipitate a brown solid. This crude product was recrystallized once from ether and once from alcohol and water to give 3.0 g. of pale-yellow crystals, m.p. 98–99°.

Anal. Calc'd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06.

Found: C, 72.61; H, 7.64; N, 6.02.

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA AND MINIMA FOR α,β-UNSATURATED KETONES IN HEPTANE SOLUTION

COMPOUND	MAXIMA		MINIMA		REFERENCE TO PREP.
	λ mμ	$\epsilon \times 10^{-3}$	λ mμ	$\epsilon \times 10^{-3}$	
I Benzylacetophenone	238	12.4	260	1.10	(6)
	280	1.50			
II Benzalacetophenone	226	12.1	241	4.85	(7)
	299	23.9			
III Benzalacetone	224.5	11.2	223	10.8	(8)
	279	21.6	234	1.37	
IV Ethylideneacetophenone	250	17.5			(2)
V Benzalacetophenone, α-N-methylbenzylamino-	248	17.3	224	12.1	(4b)
	286	16.7	267	14.6	
	392	1.55	343	1.14	
VI Benzalacetophenone, α-morpholino-	249	16.7	225	10.6	(9)
	278	15.7	267	15.1	
	365	1.48	234	1.28	
VII Benzalacetone, α-morpholino-	267	8.57	242	7.56	(10)
VIII Ethylideneacetophenone, α-morpholino-	242	16.9	268	1.25	new
	282	1.50	299	0.64	
	329	0.97			
IX Benzalacetophenone, β-benzylamino-	241	13.7	225	11.1	(11)
	346	19.2	283	1.25	
X Benzalacetophenone, β-morpholino-	245	16.4	225	11.7	(9)
	328	13.0	284	3.44	
XI Benzalacetone, β-morpholino-	236	9.57	263	5.13	new
	295	10.5			
XII Ethylideneacetophenone, β-morpholino-	242	8.45	222	6.00	(10)
	320	17.3	268	1.40	
XIII Ethylideneacetone, β-amino-	285	6.12	225	0.19	(12)
XIV Benzalacetophenone, p-dimethylamino-	254	17.6	226	6.45	(13)
	385	33.3	297	1.82	
XV Benzalacetone, p-dimethylamino-	243	10.6	280	2.15	(14)
	360	29.4			

β-Morpholinobenzalacetone, (XI). A method similar to that reported by Andre (5) for such compounds was used here. Phenylacetylacetylene (0.8 g.) was dissolved in 5 ml. of ether and the solution cooled in an ice-bath. To this was added 0.8 g. of morpholine. The mixture was allowed to stand in the ice-chest for a week. The reaction mixture was diluted with ether, washed several times with water, dried and evaporated. The residual dark product was recrystallized from petroleum ether and from heptane to give 0.4 g. of colorless crystals, m.p. 83–85°.

Anal. Calc'd for $C_{14}H_{17}NO_2$: C, 72.71; H, 7.41; N, 6.05.

Found: C, 72.90; H, 7.25; N, 5.90.

Absorption spectra measurements. These studies were made with highly purified (15) heptane-from-petroleum solutions of compounds (I)–(XV), using a model DU Beckman spectrophotometer. The relative transmission of our heptane when compared with distilled water was 72% at 220 mμ, 90% at 235 mμ and 100% at 265 mμ. Care was taken to avoid the exposure of the dilute solutions to sunlight and all measurements were made within two hours of their preparation from fresh materials.

The wave-length and molar extinction coefficients for the maxima and minima in the spectrum of each compound are recorded in Table I, and the complete spectra, measured at 1–5 mμ intervals over the range of 220–600 mμ are represented by the curves in Figures 1, 2, 3 and 4.

In the case of benzalacetophenone (II) exposure to various amounts of light and aging of the solutions in the dark were studied to determine to what extent these factors affect the ultraviolet absorption spectra. See Figure 5.

Discussion of the spectra and structure. This study has resulted in a series of spectra that should be of use in helping to identify the structures of new, related compounds.[2]

In the parent α, β-unsaturated ketone series, Figure 1, the presence of a phenyl group on the β-carbon atom is of more importance than its location on the carbonyl carbon in providing for the longest possible ionic structure with oxygen carrying a charge.
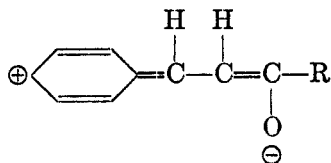
The spectra of ethylideneacetophenone (IV) was found to be quite similar to that of phenylvinyl ketone (λ max., 247.5 mμ, ϵ, 10,500), as reported by Bowden, *et al.* (16). These structures differ only by a β-methyl group which would not be expected to show a bathochromic effect of more than about 11 mμ (17). Our spectra curves for benzalacetone, benzalacetophenone and their *p*-dimethylamino derivatives were nearly identical with those reported by Alexa (18) using the same type of solvent but a different instrument, see Figures 1 and 4.

The α-amino-α,β-unsaturated ketones, Figure 2, for purposes of discussion, may be divided into four classes, see Table II. All of the known members of this series have been derived from secondary amines. The ionic structures that one can write for any of the α-amino-α,β-unsaturated ketones can be expected to be less stable than those possible for the β-amino ketones which are discussed later.

Although there are no known examples of Class I as yet, we would predict that they would absorb light at shorter wave lengths than their β-amino isomers.

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[2] For example see, Cromwell and Eby, (to be published soon), who report that 2-morpholino- and 2-piperidino-4,4-dimethyl-1-keto-1,4-dihydronaphthalene, which are closely related structurally to α-morpholinoethylideneacetophenone (VIII), show maxima at 248–250 mμ, 290–289 mμ, 299–298 mμ and 321–332 mμ.

Class II compounds might be expected to give the general type of absorption shown by compound (VII), since none of the various possible ionic structures would seem to be particularly stable.   In Classes III and IV it becomes possible to have ionic structures in which nitrogen may become positive and oxygen negative at the same time.   This factor can be expected to enhance the stability of these ionic structures.

Since in Classes III and IV we can also expect the existence of the ionic structures described for Classes I and II it is not surprising that the former show maxima in at least three general areas, (240–250; 270–290; and 330–395 mμ). In Class IV the presence of phenyl groups on both the β-carbon and the carbonyl carbon provides for the longer conjugated unsaturated ionic structure in which
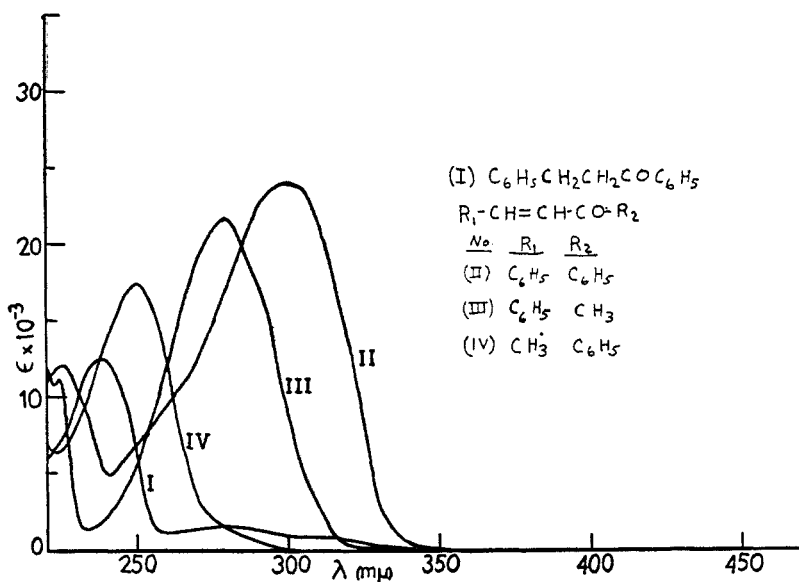
FIG. 1.   ABSORPTION SPECTRA OF UNSATURATED KETONES

both nitrogen and oxygen carry a charge.   Thus these compounds absorb light near the visible range although the intensity is low because the required ionization is inhibited by the energy of the Kekulé resonance of the benzene rings which must be overcome.   It is this low, broad-banded maximum at relatively long wave-lengths that is especially typical of the α-amino-α,β-unsaturated ketones, with aryl groups attached to the carbonyl carbon.

The β-amino-α,β-unsaturated ketones, Figure 3, show a short wave-length band between 240 and 250 mμ, and a longer wave-length band above 320 mμ if they are also aryl ketones.   Our spectrum for β-morpholinoethylideneacetophenone (XII) is very similar to those reported by Bowden, et al. for the β-amino-, β-ethylamino- and β-diethylamino-phenylvinyl ketones (16).

In the β-amino-α,β-unsaturated ketone series the presence of a phenyl group

TABLE II

CLASSES OF α-AMINO-α,β-UNSATURATED KETONES

CLASS		TYPE STRUCTURE (TYPE MAXIMA, $m\mu$)	IMPORTANT IONIC STRUCTURES	EXAMPLES IN TABLE I
No.	Unsatu-ration			
I	α,β-	(broad, 250?)	and	None known
II	$\alpha,\beta,\gamma,\delta$-	(broad 267)	and	(VII)
III	$\alpha,\beta,\alpha',\beta'$-	(242; 282; 329)		(VIII)
IV	$\alpha,\beta,\alpha',\beta',\gamma,\delta$-	(248; 286; 392)		(V), (VI)

on the β-carbon has a smaller bathochromic effect on the longer wave-length absorption than in the parent unsaturated ketone series.   This may be accounted
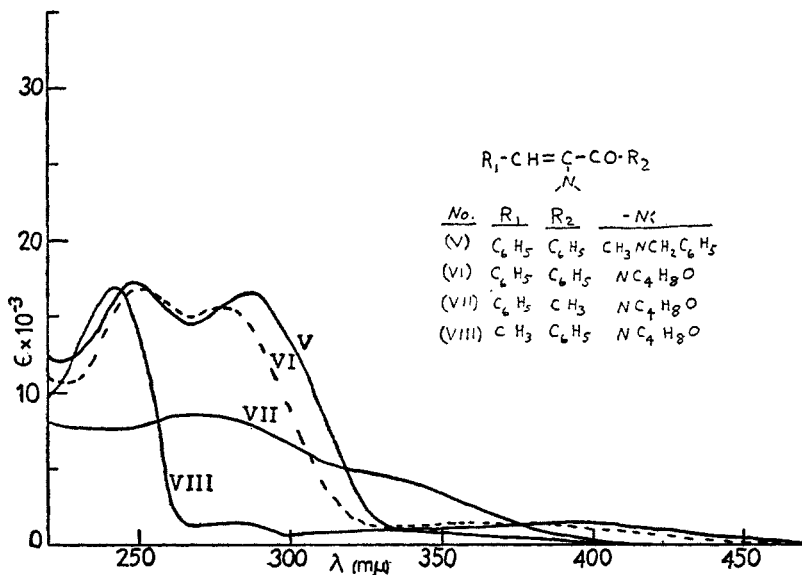

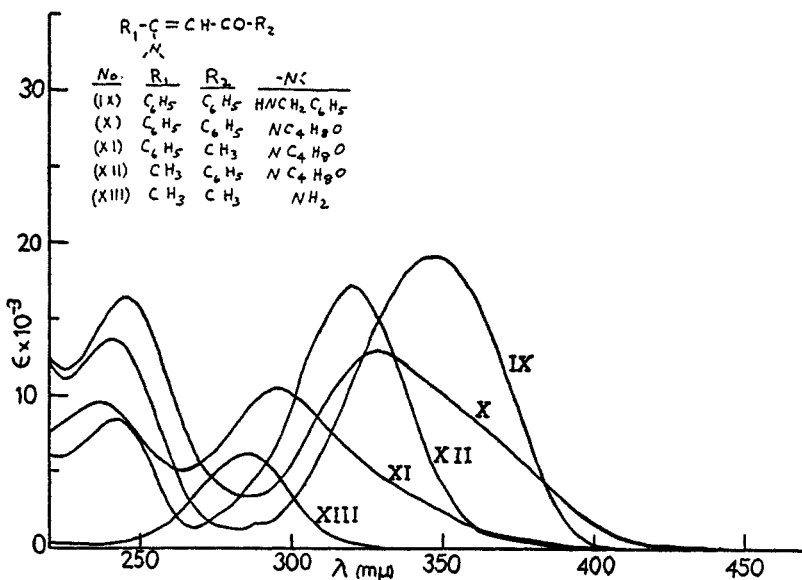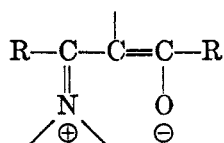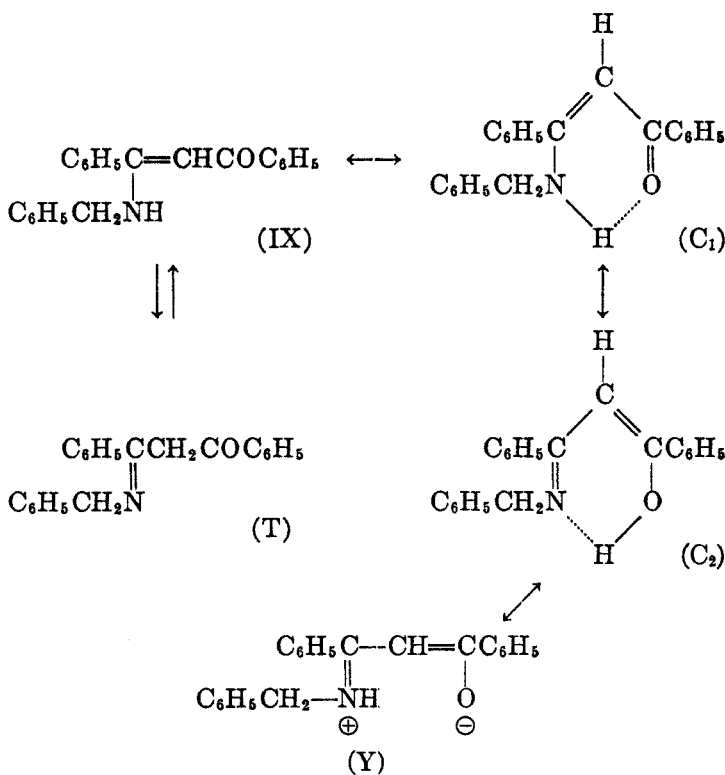FIG. 2. ABSORPTION SPECTRA OF α-AMINO UNSATURATED KETONES

FIG. 3. ABSORPTION SPECTRA OF β-AMINO UNSATURATED KETONES

for by observing that the longer wave-length absorption in this series would seem to be associated with the following ionic form.

$$R-C-\overset{|}{C}=C-R$$
$$\overset{\|}{N}\qquad\overset{|}{O}$$
$$\diagup{\overset{\oplus}{}}\diagdown\qquad\ominus$$

The replacement of an alkyl group by a phenyl group on the carbonyl carbon in this series seems to result in a bathochromic effect on the longer wave-length absorption of from 33–46 mμ (see also the results of Bowden, et al. (16)). The effects on the longer wave-length spectra of change in the β-amino group will depend on the type of variation. Increased basic strength of the groups should enhance absorption in this region. Introduction of arylamino groups may be expected to provide for interaction between the α,β-unsaturated ketone chromophore and the aromatic ring of the amine (16). The substitution of a simple NH$_2$ group or a primary amino group, RNH, for a secondary amino radical might be expected to increase the absorption at the longer wave-lengths if other factors, such as basic strength, remained unchanged.

The general shapes of the curves, Figure 3, for (IX) and (X) are the same but the substitution of a primary amino group of greater basic strength for the morpholino group has produced a noticeable bathochromic effect on the longer wave-length absorption. The tautomerism (IX)⇌(T) would be expected to divide such compounds into two insulated, shorter unsaturated systems. This tauto-

merism would not be expected to change appreciably the absorption near 240–250 mμ ascribed to the chromophore C_6H_5CO, but would be expected to reduce
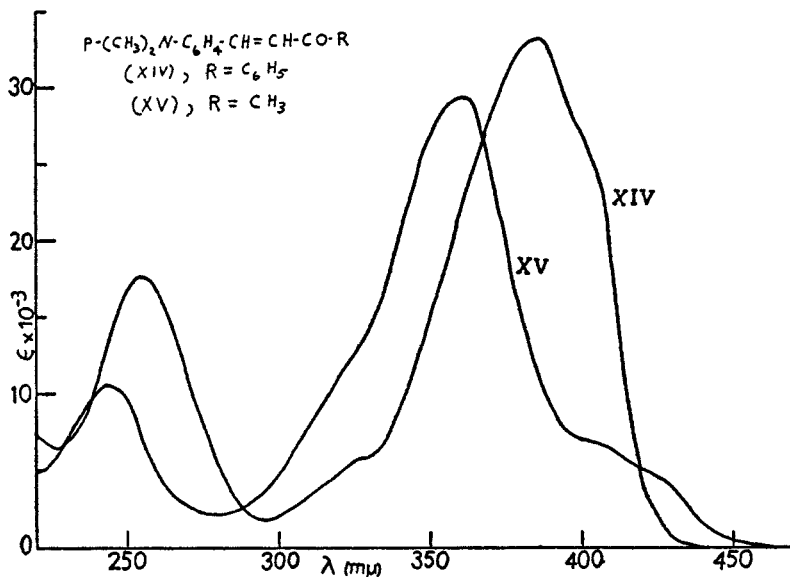

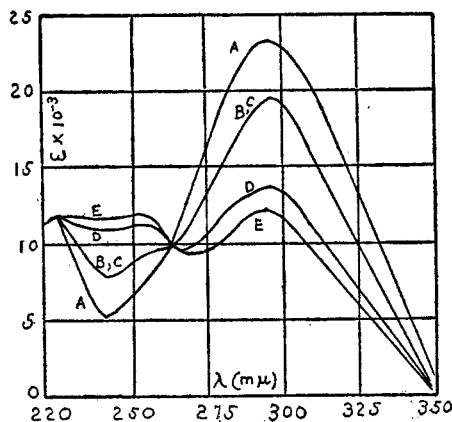FIG. 4. ABSORPTION SPECTRA OF β-(p-DIMETHYLAMINOPHENYL) UNSATURATED KETONES

FIG. 5. IRRADIATION EFFECTS ON ULTRAVIOLET ABSORPTION SPECTRUM OF A 0.000025 M. SOLUTION OF BENZALACETOPHENONE IN HEPTANE

(A), 80 minutes after preparation, dark storage. (B), after a further 110 minutes in ordinary laboratory daylight, storage in glass volumetric flask. (C), no significant changes after a further dark storage of 30 minutes. (D), after a further 5 minutes of direct sunlight, quartz cell storage. (E), after an additional 20 minutes in direct sunlight, quartz cell storage.

the absorption near 320–325 mμ ascribed to the ionic structure (Y). Conversely, hydrogen-bonding through chelation (IX)$\leftrightarrow$(C$_1$)$\leftrightarrow$(C$_2$) might be expected to

enhance the stability of the ionic structure (Y). It would seem that there is little or no tendency for the tautomerism, (IX)⇌(T).

The experiments, Figure 5, on the irradiation of the solutions of benzalacetophenone (chalkone) show that there is a great change in the spectrum after exposure to sunlight. That this is due to the dimerization reported by Stobbe and Bremer (19) seems likely. The decrease in the absorption at 299 mμ, and the increased absorption at shorter wave-lengths (240–250 mμ) may easily be due to the formation of the dimer, which still has the carbonyl groups in conjugation with the benzene nuclei.

It would seem important to protect the dilute solutions of all α,β-unsaturated ketones from direct sunlight before making absorption spectra studies. Such precautions were taken in the present investigation.

SUMMARY

1. The preparation of α-bromo- and α-morpholino-ethylideneacetophenone, and of β-morpholinobenzalacetone have been described.

2. The ultraviolet absorption spectra of fifteen unsaturated ketones or their amino derivatives have been measured in heptane solution over the range of 220–600 mμ.

3. The α-amino-α,β-unsaturated ketones have been classed according to the nature of the ionic resonance or excited structures possible and the characteristic maxima to be expected for each class.

4. Several β-amino-α,β-unsaturated ketones have been studied and the bathochromic effects of phenyl and methyl substituents observed.

5. The possibility of tautomerism and chelation with β-(primary amino)-α,β-unsaturated ketones was discussed from the standpoint of the absorption spectrum of such a compound.

6. The effects of sunlight irradiation on solutions of benzalacetophenone have been studied using ultraviolet absorption spectra measurements and evidence of dimerization as previously shown by Stobbe and Bremer has been obtained.

LINCOLN, NEBRASKA.

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