

## Study of substituent effects in substituted dibenzal acetones

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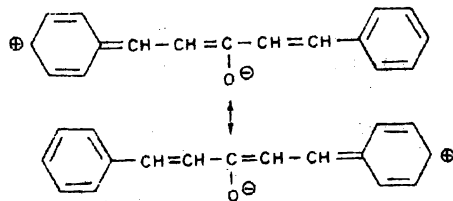
**Abstract :** The present work involves a detailed study of the ultra-violet absorption spectra of various substituted dibenzylidene ketones derived from acetone, ethyl methyl ketone, diethyl ketone, cyclopentanone and cyclohexanone by condensing with several *meta*- and *para*-substituted benzaldehydes in *n*-hexane and in ethanol to ascertain the transition dominant in these solvents. These ketones exist as equilibrium mixtures of *s-cis*, *cis* and *s-trans*, *trans* conformations. The ultraviolet absorption spectra of the ketones exhibit two bands due to  $\pi^* \leftarrow \pi$  transition around 250 and 320 nm. The 320 nm band is prominent in all the cases. There is no indication of  $\pi^* \leftarrow n$  transition in any of the spectra.

The 320 nm band is structureless in all the cases except those shown by the dibenzylidene ketones derived from cyclopentanone in hexane. Therefore it can be inferred that the dibenzylidene ketones derived from all the ketones except those derived from cyclopentanone are non-planar.

**Keywords :** Dibenzoyl acetone, substituent effect, absorption spectra.

$\alpha,\beta$ -Unsaturated carbonyl compounds exist in *s-cis* and *s-trans* forms. Lutz and co-workers<sup>1</sup> have shown that significant differences exist in the spectra of the *cis*- and *trans*-chalcone structures. These forms can be thought to consist of two different independently non-conjugated chromophoric systems, namely benzoyl and cinnamoyl groups<sup>2</sup>. Thus one might expect two independent characteristic band groups for these groups of chromophores in chalcones.

Two structureless absorption bands were observed for dibenzylideneacetone in ethanol and in cyclohexane, viz. at 229 nm and 320 nm<sup>3</sup>. These absorptions were attributed to  $\pi^* \leftarrow \pi$  transition and conjugation in the molecule is represented below is responsible for the absorption.



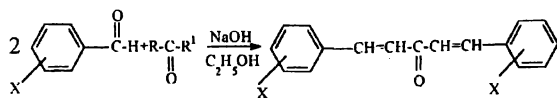
The present work summarizes the result of a detailed and exhaustive research carried out on the ultraviolet

absorption spectra of several *meta*- and *para*-substituted dibenzylidene ketones derived from acetone, ethylmethyl ketone, diethyl ketone, cyclopentanone and cyclohexanone.

### Experimental

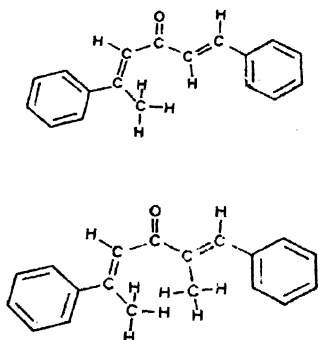
**Preparation of 1,5-diphenyl-1,4-pentadien-3-one :** Acetone (1 ml; 0.01 mol), benzaldehyde (2.02 ml; 0.02 mol), ethanol (20 ml; 95%) and aqueous sodium hydroxide (15 ml; 10%) were placed in a 125 ml Erlenmeyer flask. The contents were shaken at room temperature for 15 min, until no more solid separated. Then the flask was cooled in ice and the product was collected by filtration. The crude product was washed with ice-cold, 10 ml portions of 95% ethanol. The product was then dried and recrystallized from aqueous ethanol. The product melted at 110–111 °C (lit. m.p. 112–113 °C).

**Preparation of several *meta*- and *para*-substituted dibenzylidene ketones :** Various *meta*- and *para*-substituted dibenzylidene ketones were prepared by condensing *meta*- and *para*-substituted benzaldehyde with appropriate ketone like acetone, ethyl methyl ketone, diethyl ketone, cyclopentanone and cyclohexanone in the presence of base in the alcoholic medium.



## Results and discussion

In all the spectra (in ethanol and hexane) the principal absorption band is only due to  $\pi^* \leftarrow \pi$  transition and that occurs around 250 and 320 nm. The 320 nm absorption is prominent in all the cases. There is no indication of  $\pi^* \leftarrow n$  transition in any of the spectra. The 320 nm band is structureless in all the cases except those shown in *n*-hexane by the dibenzylidene ketones derived from cyclopentanone. In a planar system the band due to  $\pi^* \leftarrow \pi$  transition is normally polarized and exhibits fine structure in the band.



The dibenzylidene ketones derived from all the ketones except those derived from cyclopentanone are non-planar. In the case of dibenzylidene ketones derived from acetone, ethyl methyl ketone and diethyl ketone the possible stable conformations are *s-cis*, *cis* and *s-cis, trans*. In the case of dibenzylidene ketones formed from ethyl methyl ketone and diethyl ketone the strain in the *s-cis, trans* conformation of dibenzylidene acetone due to the proximity of one methyl group to the  $\beta$ -hydrogen of the other olefinic system in one case and the two methyl groups of the two olefinic systems being close to each other in the other case. This is shown in above.

The existence of large steric interaction in the case of the *s-cis, trans* conformations derived from ethyl methyl ketone and diethyl ketone, it is to be expected that the two styryl moieties in these cases will assume mostly the *s-cis, cis* conformations. Even in this conformation the steric strain is larger than that existing in the corresponding conformation of dibenzylideneacetone. Hence we can

assume that the two styryl moieties in the *s-cis* conformations of the dibenzylidene ketones from ethyl methyl ketone and diethyl ketone will twist to a larger extent than that happens in the corresponding case of dibenzylidene acetone. Therefore their torsion angles should also be greater than  $22^\circ$  in these cases. Hence there is an ample reason to believe that the principal band around 320 nm in all these compounds is structureless.

The Hammett correlation is made with  $\sigma$  and  $\sigma^*$  constants in the region of principal maximum of absorption for all the dibenzylidene ketones derived from acetone, ethyl methyl ketone and shown Table 1. Correlations employing  $\lambda_{\max}$  values obtained in ethanol and in hexane solutions separately and with  $\Delta\lambda_{\max}$  ( $\lambda_{\max}(\text{ethanol}) - \lambda_{\max}(\text{hexane})$ ) values are extremely insignificant and are given below.

Table 1. UV absorption maxima

(a)  $\lambda_{\max}$  (nm) of 1,5-di (*m*- or *p*-substitutedphenyl)-1,4-pentadien-3-ones :

Sl. no.	Substituent	Ethanol	Hexane
1.	H	326	317.5
2.	<i>m</i> -Br	327	312
3.	<i>m</i> -Cl	328	312.5
4.	<i>p</i> -Cl	304	318
5.	<i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub>	322	321
6.	<i>p</i> -CH <sub>3</sub>	307	304
7.	<i>o</i> -OCH <sub>3</sub>	330	341
8.	<i>p</i> -OCH <sub>3</sub>	345	325
9.	<i>m</i> -NO <sub>2</sub>	267.5	260
10.	<i>p</i> -NO <sub>2</sub>	317	300

(b)  $\lambda_{\max}$  (nm) of 1,5-di (*m*- or *p*-substitutedphenyl)-2-methyl-1,4-pentadien-3-ones :

1.	H	288.8	276
2.	<i>m</i> -Br	279	278
3.	<i>m</i> -Cl	268	277
4.	<i>p</i> -Cl	287	283
5.	<i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub>	327	332
6.	<i>p</i> -CH <sub>3</sub>	306	293
7.	<i>o</i> -OCH <sub>3</sub>	349	351
8.	<i>p</i> -OCH <sub>3</sub>	341	230.5
9.	<i>m</i> -NO <sub>2</sub>	247	206
10.	<i>p</i> -NO <sub>2</sub>	270	271

The correlations generated for 1,5-di (*m*- or *p*-substitutedphenyl)-1,4-pentadiene-3-ones in ethanol and in hexane are given in eqs. (1) to (6)

$$\lambda_{\max} (\text{ethanol}) = -19.87 \sigma + 319.11 \quad (1)$$

$$(r = -0.470, s = 0.071, n = 10)$$

$$\lambda_{\max} (\text{hexane}) = -31.21 \sigma + 312.66 \quad (2)$$

$$(r = -0.652, s = 0.09, n = 10)$$

$$\Delta\lambda_{\max} = 4.89 \sigma + 10.413 \quad (3)$$

$$(r = 0.369, s = 0.056, n = 10)$$

$$\lambda_{\max} (\text{ethanol}) = -11.11 \sigma + 317.53 \quad (4)$$

$$(r = -0.40, s = 0.061, n = 10)$$

$$\lambda_{\max} (\text{hexane}) = -22.42 \sigma + 305.19 \quad (5)$$

$$(r = -0.634, s = 0.096, n = 10)$$

$$\lambda_{\max} = 2.96 \sigma + 11.03 \quad (6)$$

$$(r = 0.35, s = 0.096, n = 10)$$

The correlations generated for 1,5-di (*m*- or *p*-substitutedphenyl)-2-methyl-1,4-pentadiene-3-ones in ethanol and in hexane are given in eqs. (7) to (12)

$$\lambda_{\max} (\text{ethanol}) = -47.49 \sigma + 303.22 \quad (7)$$

$$(r = -0.681, s = 0.104, n = 10)$$

$$\lambda_{\max} (\text{hexane}) = -61.78 \sigma + 284.48 \quad (8)$$

$$(r = -0.635, s = 0.061, n = 10)$$

$$\Delta\lambda_{\max} = 7.392 \sigma + 8.894 \quad (9)$$

$$(r = 0.302, s = 0.047, n = 10)$$

$$\lambda_{\max} (\text{ethanol}) = -36.351 \sigma + 293.10 \quad (10)$$

$$(r = -0.814, s = 0.126, n = 10)$$

$$\Delta\lambda_{\max} (\text{hexane}) = -27.55 \sigma + 279.807 \quad (11)$$

$$(r = -0.488, s = 0.076, n = 10)$$

$$\Delta\lambda_{\max} = 4.27 \sigma + 9.922 \quad (12)$$

$$(r = 0.259, s = 0.039, n = 10)$$

The poor correlations exhibited by the above equations are fundamentally due to the nature of the systems investigated which are not of uniform character to transmit electronic effects of substituents as demanded by Hammett equations. The Hammett equation is unfortunately unsuccessful in the above cases. The peculiarity of the systems having two *s-cis* double bonds may in some way be responsible for the break down of Hammett equations in these cases due to ineffective transmission of substituent effects. The correlations obtained for substituted 2,6-dibenzylidene cyclohexanones (eqs. (13) to (18)) and substituted 2,5-dibenzylidene cyclopentanones (eqs. (19) to 24)) are given below.

Table 2. UV absorption maxima

(a) Substituted 2,6-dibenzylidene cyclohexanones :

Sl. no.	Substituent	Ethanol	Hexane
1.	H	320	317
2.	<i>m</i> -Br	325.5	324
3.	<i>m</i> -Cl	325.0	314.5
4.	<i>p</i> -Cl	326.5	323.0
5.	<i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub>	341.5	378.5
6.	<i>p</i> -CH <sub>3</sub>	333.5	327.0
7.	<i>o</i> -OCH <sub>3</sub>	340.0	331.5
8.	<i>p</i> -OCH <sub>3</sub>	359.0	330
9.	<i>m</i> -NO <sub>2</sub>	339.5	332.5
10.	<i>p</i> -NO <sub>2</sub>	318.0	311.0

(b) Substituted 2,5-dibenzylidene cyclopentanones :

1.	H	352	336.5
2.	<i>m</i> -Br	360	345.0
3.	<i>m</i> -Cl	348	336.0
4.	<i>p</i> -Cl	361	342.5
5.	<i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub>	478.5	475.0
6.	<i>p</i> -CH <sub>3</sub>	371.0	344.5
7.	<i>o</i> -OCH <sub>3</sub>	377.5	358.0
8.	<i>p</i> -OCH <sub>3</sub>	391.0	359.0
9.	<i>m</i> -NO <sub>2</sub>	337.5	333.6
10.	<i>p</i> -NO <sub>2</sub>	360.0	338.5

Correlation equation for 2,6-dibenzylidene cyclohexanones are given in eqs. (13) to (18).

$$\lambda_{\max} (\text{ethanol}) = 11.95 \sigma + 328.3 \quad (13)$$

$$(r = -0.257, s = 0.037, n = 10)$$

$$\lambda_{\max} (\text{hexane}) = 0.51 \sigma + 319.21 \quad (14)$$

$$(r = 0.015, s = 0.02, n = 10)$$

$$\Delta\lambda_{\max} = -12.22 \sigma + 9.5728 \quad (15)$$

$$(r = -0.593, s = 0.073, n = 10)$$

$$\lambda_{\max} (\text{ethanol}) = -1.88 \sigma + 327.590 \quad (16)$$

$$(r = -0.064, s = 0.010, n = 10)$$

$$\lambda_{\max} (\text{hexane}) = 5.49 \sigma + 320.56 \quad (17)$$

$$(r = 0.264, s = 0.042, n = 10)$$

$$\Delta\lambda_{\max} = -7.95 \sigma + 7.342 \quad (18)$$

$$(r = -0.611, s = 0.096, n = 10)$$

$\lambda_{\max}$  value of substituted 2,5-dibenzylidene cyclopentanones :

$$\lambda_{\max} (\text{ethanol}) = -110.8 \sigma + 354.33 \quad (19)$$

$$(r = -0.630, s = 0.099, n = 10)$$

$$\lambda_{\max} (\text{hexane}) = -18.32 \sigma + 344.66 \quad (20)$$

$$(r = -0.534, s = 0.83, n = 10)$$

$$\Delta\lambda_{\max} = -16.96 \sigma + 19.43 \quad (21)$$

$$(r = -0.64, s = 0.101, n = 10)$$

$$\lambda_{\max} (\text{ethanol}) = -62.56 \sigma^+ + 347.39 \quad (22)$$

$$(r = -0.674, s = 0.106, n = 10)$$

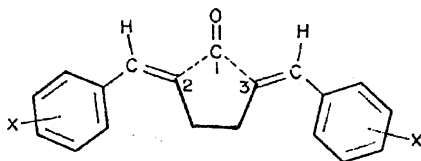
$$\lambda_{\max} (\text{hexane}) = -13.25 \sigma^+ + 342.84 \quad (23)$$

$$(r = -0.599, s = 0.094, n = 10)$$

$$\Delta\lambda_{\max} = 5.092 \sigma^+ + 31.813 \quad (24)$$

$$(r = 0.052, s = 0.008, n = 10)$$

The Hammett equation is unfortunately unsuccessful in the above cases also. The peculiarity of the systems having two *s-cis* double bonds in some way be responsible for the break down of Hammett equation in these cases, due to ineffective transmission of substituent effects.



The principal band around 320 nm exhibits fine structure. This may be due to the low Bayer's strain (0.44') that exist in cyclopentane ring and hence the whole molecule assumes predominantly planar brief case structure with only *s-cis*, *cis* conformation. The possibility of other conformations (*s-cis*, *trans* and *s-trans*, *trans*) is totally ruled out in this case.

#### Conclusion :

Ultraviolet spectra of several substituted dibenzylidene ketones were recorded. The ultraviolet absorption spec-

tra of these ketones exhibit two bands due to  $\pi^* \leftarrow \pi$  transition around 250 and 320 nm. The 320 nm band is prominent in all the cases. There is no indication of  $\pi^* \leftarrow n$  transition in any of the spectra. All the spectra were recorded in ethanol and in hexane solutions.

The 320 nm band is structureless in all the cases except those shown by the dibenzylidene ketones derived from cyclopentanone in hexane. Therefore it can be inferred that the dibenzylidene ketones derived from all the ketones except those derived from cyclopentanone are non-planar.

The Hammett correlation is made with different substituent constants. The correlations are extremely insignificant.

The poor correlations exhibited by the above equations are fundamentally due to the nature of the systems investigated which are not of uniform character to transmit electronic effects of substituents as demanded by Hammett equations.

What was achieved by Hoshi, Kawashima, Okubu and Yamamota<sup>3</sup> with dibenzylideneacetone by using highly viscous medium (polyethylene matrix) or by lowering the temperature has been achieved by us at room temperature in the case of dibenzylidene derivatives of cyclopentanone. Indeed, this may be the hallmark of the present investigation.

#### References

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