

Conformations of α, β -unsaturated ketones: An IR spectroscopic study

G VENKATESHWARLU and B SUBRAHMANYAM*

Department of Chemistry, Osmania University, Hyderabad 500 007, India

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Abstract. The conformational analyses of substituted methyl styryl ketones and phenyl styryl ketones have been carried out using IR spectroscopy. The split in the C=O bands of these compounds is attributed to the existence of two conformations, viz. *s-cis* and *s-trans*, in equilibrium. The methyl styryl ketones exist predominantly in the *s-trans* form whereas phenyl styryl ketones exist in the *s-cis* form. In all the ketones studied the proportion of the *s-trans* form increases with increase in the polarity of the solvent while that of the *s-cis* form decreases. This shows that the *s-trans* form is more polar than the *s-cis*. The field effects between the C=O and C=C groups are found to be electrostatic repulsions which play a dominant role in the determination of the relative stabilities of the *s-cis* and *s-trans* forms over the steric effects and the electrostatic attractions between the carbonyl oxygen and the β -carbon.

Keywords. α, β -unsaturated ketones; split in the C=O bands; rotational isomers; polarity of the conformers; π -electron repulsions.

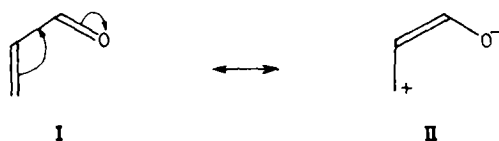
1. Introduction

The conformational analysis of α, β -unsaturated carbonyl compounds has been a subject of considerable interest and was investigated by many workers (Erskine and Waight 1960; Noack and Jones 1961; Hayes and Timmons 1968; Bowles and George 1969). The relative stabilities of the two conformers viz. *s-cis* and *s-trans* are considered to be determined by two factors (a) field effects between the C=O and C=C groups and (b) steric effects between the substituents present on the carbonyl and ethylenic carbon atoms.

Although the influence of the steric effects on the relative stabilities of the two conformers has fully been explored, the exact nature of the field effects is not clearly known. The field effects are considered by Erskine and Waight (1960) and Noack and Jones (1961) as electrostatic attractions between C=O, C=C dipoles arising from the resonance in the enone moiety (I, II) which stabilise the *s-cis* form. Hayes and Timmons (1968) and Bowles and George (1969) are of the opinion that they are electrostatic repulsions between the π electrons of the C=O and C=C bonds which destabilize the *s-cis* form.

It was, therefore, considered worthwhile to probe the exact nature of the field effect and its influence on the relative stabilities of the *s-cis* and *s-trans* forms. To accomplish

* For correspondence



this the methyl styryl ketones and phenyl styryl ketones with electron-releasing groups in the *p*-position of the styryl ring were chosen.

2. Experimental

2.1 Materials

The compounds were prepared by aldol condensation of substituted benzaldehydes and acetone or acetophenone in 1:1 molar ratios in alkaline media in ethanol (Vogel 1980). The solids separated were purified and recrystallised twice from methanol and were TLC-pure. The solvents used in the study were purified by methods available in literature and freshly distilled before use and only the middle fractions were collected.

2.2 Measurement of the spectra

The IR spectroscopic technique was chosen for this study as the vibrational frequencies of the C=O bands are useful not only in distinguishing between the two conformers but also for indicating the relative electron densities of the C=O bonds.

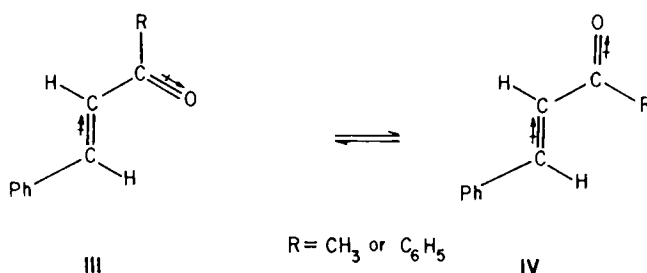
The IR spectra of equimolar solutions (M/20) of methyl styryl ketones in solvents of varied dielectric constants were recorded at slow speed on a Perkin-Elmer 337 and those of phenyl styryl ketones on a Shimadzu 400 grating double beam spectrophotometer at 28°C using matched NaCl cells of 1 mm path length. The relative proportions of the *s-cis* and *s-trans* forms were estimated from the relative apparent optical densities of the C=O bands of the two forms (Erskine and Waight 1960; Kossanyi 1965).

3. Results and discussion

All the compounds exhibited doublet C=O bands in all the solvents studied viz. CCl₄, CHCl₃ and CH₂Cl₂. The intensities of the lower frequency bands increased with increase in polarity of the solvent and those of the higher frequency bands decreased. This pattern of intensity variation of the C=O bands is analogous to that observed in the case of dibenzylideneacetone (Venkateshwarlu and Subrahmanyam 1987), which was shown to be due to rotational isomerism.

The split in the C=O bands may, therefore, be attributed to the existence of two rotamers viz. *s-cis* (III) and *s-trans* (IV) in equilibrium. From the fact that the more polar forms are stabilised in polar solvents and the less polar forms in non-polar solvents, the higher frequency bands were assigned to the *s-cis* and the lower frequency bands to the *s-trans* forms.

Of the two forms, viz. *s-cis* and *s-trans*, the latter is more polar than the former. For the C=O dipole in the *s-trans* form is reinforced by the C=C dipole whereas it is



opposed by it in the *s-cis* form (III and IV). This is consistent with the calculated dipole moments of the *s-cis* (3.25 D) and *s-trans* (3.80 D) forms of the methyl styryl ketone (Bentley *et al* 1949).

The band assignments are also consistent with those made by Hayes and Timmons (1968) on the basis of solvent shifts of the C=O bands and by Erskine and Waight (1960) on the basis of the band separations and the intensity ratios of the C=O and C=C bands.

3.1 Conformations of the molecules and their stabilities

From the relative intensities of the *s-cis* and *s-trans* C=O bands, it is clear that the predominant conformer in methyl styryl ketone is the *s-trans*. It is however *s-cis* in phenyl styryl ketone (figures 1 & 2).

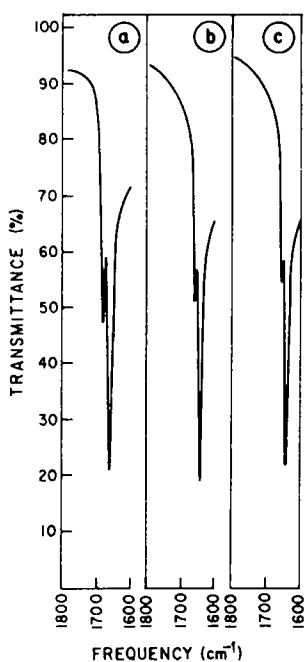


Figure 1.

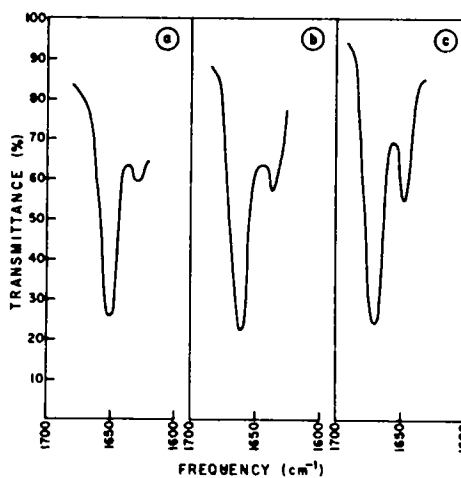
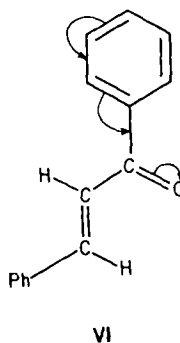
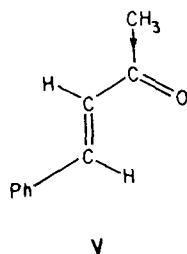


Figure 2.

Figure 1. The C=O bands of methyl styryl ketones in CCl_4 . Substituent in the *p*-position is (a) $-\text{N}(\text{CH}_3)_2$, (b) $-\text{OCH}_3$ and (c) $-\text{H}$.

Figure 2. The C=O bands of phenyl styryl ketones in CCl_4 . Substituent at the *p*-position is (a) $-\text{N}(\text{CH}_3)_2$, (b) $-\text{OCH}_3$ and (c) $-\text{H}$.



It is interesting to note here that cinnamaldehyde is exclusively stabilised in the *s-trans* form and the stability of this form is slightly decreased in methyl styryl ketone and largely in the phenyl styryl ketone.

The destabilisation of this form is likely to be due to the steric effects of the methyl or phenyl groups in the *s-trans* form. It was shown by Winecoff and Boykin (1972) that the steric effect due to the methyl group is very small and it is equal in both the *s-cis* and *s-trans* forms. The steric effect due to the phenyl group however is larger in the *s-cis* form than in the *s-trans* form (Perjessy 1969; Rajasekaran and Gnanasekaran 1987). If steric effects are important in any way in the relative stabilisation of the two forms, the methyl group should not have any effect on the stabilities and the phenyl group should destabilise the *s-cis* form. These groups, however, destabilise the *s-trans* form and stabilise the *s-cis* form as compared to cinnamaldehyde.

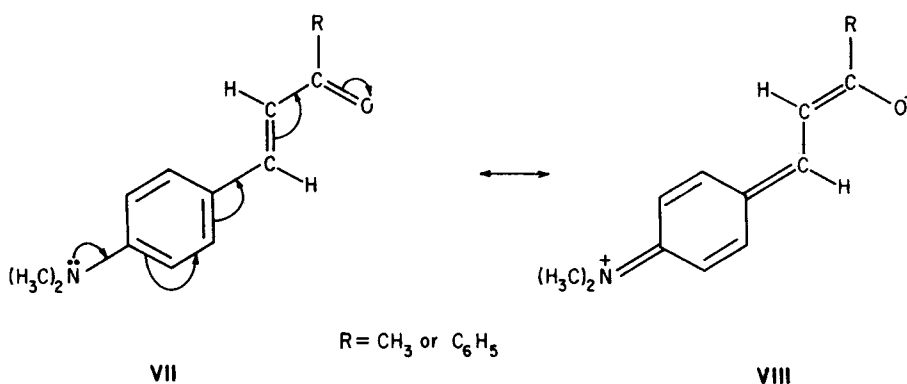
The lower stability of the *s-trans* form in phenyl styryl ketone was earlier attributed by Hayes and Timmons (1968) to the repulsions between the two phenyl rings in this form. If this were true the phenyl vinyl ketone which does not contain two phenyl rings should prefer the *s-trans* form. But Kossanyi (1965) showed that it exists predominantly in the *s-cis* form.

In the absence of steric effects, the stabilisation of *s-cis* form in the styryl ketones as compared to cinnamaldehyde may be attributed to field effects. It may be (i) the decrease in the π -electron repulsion of the C=O and C=C bands, or (ii) increase in the electrostatic attraction between the β -carbon atom and the carbonyl oxygen, both changes resulting from the polarisation of the C=O bond by the hyperconjugation of the methyl group (V) or the mesomeric effect of the phenyl group (VI).

The two factors (i) and (ii), however, can be distinguished by the introduction of electron-releasing substituents into the styryl ring. The mesomeric effect of these groups not only decreases the π -electron densities of the C=O and C=C bonds, but also neutralises the positive charge on the β -carbon atom (VII, VIII).

If the π -electron repulsions of the C=O and C=C bonds are responsible for the relative stabilities of the two forms, the electron releasing groups should stabilise the *s-cis* form as compared to the parent ketone as π -electron densities of C=O and C=C bonds are decreased by these substituents.

On the other hand, if electrostatic attractions are responsible for the relative stabilities of the two conformers electron-releasing groups should destabilise the *s-cis*



form as compared to the parent ketone, as the positive charge on the β -carbon atom is neutralised by the mesomeric interactions of the substituents, which reduces the electrostatic attractions between the carbonyl oxygen and β -carbon atom.

The ratios of the intensities of the *s-cis*/*s-trans* carbonyl bands of both methyl styryl ketone and phenyl styryl ketone are lower than their substituted derivatives and are in the order $\text{N}(\text{CH}_3)_2 > \text{OCH}_3 > \text{H}$ (table 1). This indicates that electron-releasing substituents stabilise the *s-cis* form by decreasing the π -electron repulsions between the C=O and C=C bonds.

The results of the present investigation suggest that the field effects between the C=O and C=C groups are electrostatic repulsions and they play a significant role in determining the relative stabilities of the *s-cis* and *s-trans* forms over the steric effects and the electrostatic attractions between the carbonyl oxygen and the β -carbon.

Table 1. The C=O stretching frequencies (cm^{-1}) of some α, β -unsaturated ketones in different solvents.

Substituent	$\nu_{\text{C=O}}$					
	CCl ₄		CHCl ₃		CH ₂ Cl ₂	
	<i>s-cis</i>	<i>s-trans</i>	<i>s-cis</i>	<i>s-trans</i>	<i>s-cis</i>	<i>s-trans</i>
<i>Methyl styryl ketones</i>						
N(CH ₃) ₂	1689 (0.47)*	1666	1681 (0.43)	1661	1683 (0.40)	1663
OCH ₃	1693 (0.38)	1670	1685 (0.35)	1665	1687 (0.32)	1665
H	1697 (0.36)	1674	1689 (0.33)	1669	1692 (0.28)	1670
<i>Phenyl styryl ketones</i>						
N(CH ₃) ₂	1660 (3.64)	1638	1651 (2.90)	1626	1653 (2.72)	1630
OCH ₃	1664 (2.94)	1643	1658 (2.80)	1632	1660 (2.60)	1635
H	1670 (2.77)	1648	1663 (2.56)	1639	1665 (2.47)	1641

* Values in parentheses correspond to the ratios of the intensities of the C=O bands of *s-cis* and *s-trans* forms

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