Original Research Article

Substituents on the infrared spectra of Thiazolyl styryl ketone-Correlation analysis

Abstract

A series of *p*-substituted Thiazolyl styryl ketones were synthesized by the Claisen -Schmidt condensation of various substituted benzaldehyde with 5-acetyl-2,4-dimethyl thiazole. The IR spectra for all the chalcones were recorded and effect of substituent on the carbonyl and C=N stretching frequency is analysed.

Key words; Thiazolyl styryl ketones, chalcones, IR spectra, stretching frequency

INTRODUCTION

The infrared spectra of α,β-unsaturated ketones throw light on the conformations of such molecules[1-3]. Normally the carbonyl stretching frequencies in infrared spectra of carbonyl compounds appear at 1850-1650 cm^{-1}. The frequency of the carbonyl absorption is determined almost wholly by the nature of its immediate environment and the structure of the rest

of the molecule is of little importance unless it is such as to give rise to chelation (or) some similar effect. Thus the carbonyl frequency shifts away from the normal position in α,β-unsaturated materials and in carbonyl compounds with strongly electronegative substituents on the α-carbon atom whilst in cyclic ketones the frequency shift and its direction are related to the degree of strain of the ring[4-23]. The frequency wave number decreases with the increasing electron withdrawing tendency of the group. The force constant of C=O is evaluated by the distribution of electron density around the linkage[20,21]. Several investigations have shown that the infrared wave number shifts of "mass insensitive" stretches can be correlated with inductive and mesomeric effects[14,17] and other important physical properties[21-24]. The influence of polar effects on infrared frequencies is largely independent of mass (or) combination effects. The stretching frequency wave number is affected by inductive and Mesomeric effect of the substituent. Hence the present investigation focussed on the substituent effect onthe Infra red frequency carbonyl group inthethiazolyl styryl ketone.

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2.1PREPARATION OF CHALCONES

The ethanoic dolution of 5-Acetyl-2, 4-dimethyl thiazole (0.4049g) and 4-methylbenzaldehyde (0.3537g) is refluxed with small quantity of N/10 sodium hydroxide solution for 40 hrs. The resulting solution is poured into ice-water and the formed precipitate is filtered. The crude Chalcone is recrystallized from ethanol.

Reaction

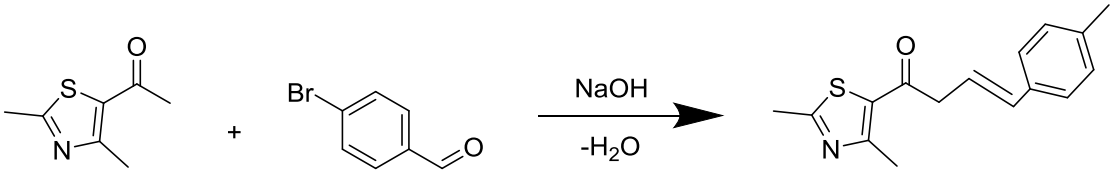

Table 1

Compound	Molecular formula	Molecular weight	Melting point(^{0}C)
1	$C_{14}H_{12}ONS$	242.35	152.2
2	$C_{14}H_{12}ONS$ Cl	282.36	165.2
3	$C_{14}H_{12}ONSBr$	321.02	173.3
4	$C_{15}H_{15}O_2NS$	273.05	158.7
5	$C_{14}H_{12}O_3N_2S$	315**.00**	170.5
6	$C_{15}H_{15}ONS$	257.35	162.2

2.2 IR MEASUREMENT

IR spectrum was recorded on AVATAR-NICOLET 330 FT-IR spectrophotometer. The sample was mixed with KBr and pallet technique was adopted to record the spectrum. The IR spectrum were recorded for liquid samples using liquid cells

Results and Discussion

In the present investigation, the compounds chosen for the study are substituted Thiazolyl styryl ketone. The infrared spectra of all the compounds are recorded in KBr disc. A number of investigations have been previously reported on the effect of substituents on the infrared carbonyl frequencies of various systems[24-25]. Normally chalcones show two carbonyl bands for *s-cis* and *s-trans* conformers in solution. Although an equilibrium mixture of different conformations of some of the chalcones may exist in solution, it is likely that only one form exist in the crystalline state. This hypothesis has been well supported by the spectral data obtained by earlier workers[25,26,]. The stretching

frequencies of carbonyl absorptions are assigned based on the assignments made by earlier workers.[27,28]

In addition to carbonyl absorption the system under investigation also shows strong band due to (>C=N) group (fig-1)

Azoles have been studied by Fuson and Josien and Jones and Moritz[29]. They found an overall range of 1598 to 1625 cm^{-1} and the latter authors have developed a equation which allows the calculation of the frequency in Thiazoles variously substituted with methyl or carbethoxy groups in different positions. Marion *et al.*[30] quote a range of 1620-1640 cm^{-1} for related systems in alkaloids.

A very substantial amount of data is available on >C=N stretching frequencies in heterocyclic ring systems. Indoles have been studied by Fuson *et al.*[30], Witkop and Marion and Vampiri[31-34]. Indole itself absorbs at 1625cm^{-1} but values as low as 16011 cm^{-1} are quoted for some derivatives. However it is doubtful if this is wholly due to substituent effects as not all cases were studied in dilute solution and it is more probable that self association is responsible for much of this shift.

2.3.3.1 Effect of substituents on carbonyl and >C=N stretching frequency

The carbonyl stretching frequencies of these Thiazolyl styryl ketones show that the lowest carbonyl frequency is observed when a powerful electron donating group is present. This may be due to the fact that electron donating group reduces the double bond character of the C=O bond and thereby lower the frequency. Even though the effectiveness of substituents are similar in *ortho*- and *para*-positions, the increase in C=O absorption frequency is attributed to the loss of coplanarity of the styryl group with the carbonyl group. The IR spectral values are furnished in Table 2. Infrared spectra of *p*-methyl substituted styryl thiazolyl ketone is shown in fig.1.

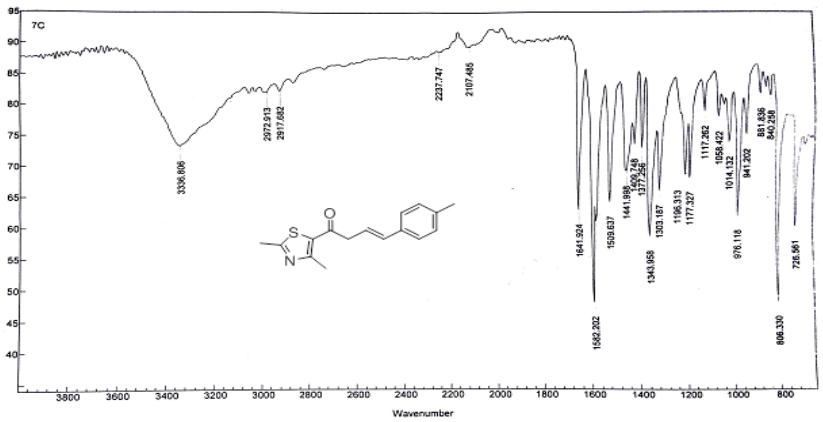

fig-1

The carbonyl and > C=N stretching vibrations are given in Table 2. The data are separately analysed through various correlation equations

involving σ and σ^+ values . The results of the statistical analysis are presented in Table 3.

Table .2

Carbonyl and >C=C< stretching frequencies of substituted Thiazolyl styryl ketone

S. No.	Substituents	$\nu_{C=O}$ (cm^{-1})	$\nu_{>C=N<}$ (cm^{-1})
1.	H	1666.47	1597.22
2	*p*-CH_3	1682.81	1582.14
3.	*p*-OCH_3	1677.57	1577.22
4	*p*-Br	1687.97	1599.72
5.	*p* -Cl	1683.93	1598.12
6	*p*-NO_2	1693.73	1607.22

All the correlation data given in Table 2 are pertaining to single parameter equation which indicates clearly that poor correlation is obtained with Hammett σ and σ^+ constants.

Table 3

Results of statistical analysis of carbonyl and >C=N< stretching frequencies of Thiazolyl styryl ketone

System	Constant for correlation	A	B	S.D	R	Substituent
$\nu_{C=O}$ (nm)	σ	1675.5	4.4017	2.9463	0.464	X = H, *p*-NO_2, *p*-OCH_3, *p*-CH_3, *p*-Br, *p* -Cl,
	σ^+	1646.6	2.340	3.0786	0.381	X = H, *p*-NO_2, *p*-OCH_3, *p*-CH_3, *p*-Br, *p* -Cl,
$\nu_{>C=C<}$ (nm)	σ	1621.1	-30.95	28.080	0.370	X = H, *p*-NO_2, *p*-OCH_3, *p*-CH_3, *p*-Br, *p* -Cl,
	σ^+	1617.5	-26.06	25.35	0.498	X = H, *p*-NO_2, *p*-OCH_3, *p*-CH_3, *p*-Br, *p* -Cl,

A = Intercept; B = Slope

The single parameter correlations are shown in Table.2. In view of the inability of some sigma constants to produce individually satisfactory correlations, it was thought worthwhile to seek multiple correlation involving σ_I and σ_R constants. The correlation equations generated are shown in Table 4

Table 4

Correlation equation with σ_I and σ_R constants

System	Correlation equation in $\nu_{C=O}$ (cm^{-1})	Substituent
Thiazolyl styryl ketone	$\nu_{C=O}$ = 1686.96 + 5.6906 σ_I + 6.5964 σ_R (R = 0.843, S.D = 2.255, n = 6)	X = H, *p*-NO_2, *p*-OCH_3, *p*-CH_3, *p*-Br, *p* -Cl,
	$\nu_{>c=n}$ = 1589.62 – 4.4813 σ_I – 53.4705 σ_R (R = 0.792, S.D = 27.14, n = 6)	

From the above table that the multiple correlation involving σ_I and σ_R constants it is observed there is a slight improvement in the R value compared with the single parameter correlation.

Conclusion

Several *para*-substituted styryl thiazolyl ketones were prepared and their infrared spectra were recorded When correlations were made for carbonyl and >C=N stretching frequencies with σ and σ^+ constants only a fair correlation was obtained.

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