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IR SPECTRAL STUDIES OF STEREOCHEMICAL 1,3-DIARYL PROPENONES

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Summary:

The infrared absorptions have been recorded of α,β-unsaturated 1,3-diaryl propenone which typify all the planar conformation. Each compound has its distinct characteristic values for frequency range, frequency separation and the intensities in terms of νC=O and νC=C. The vibrations data of α,β unsaturated ketones are best treated as out of *phase* and in *phase* coupled modes respectively.

Introduction

The four distinct alignments are possible for α,β-unsaturated ketone, 1,3-substituted diaryl propenone. To explore the solvent shift method as a tool for the identification of vibrations that include νC=C and are coupled to carbonyl, all of which show solvent sensitivity. In unsaturated ketones it is shown that s-cis and s-trans conformation are readily achieved by plotting the values of νC=C vs νC=O. The nature of this coupling is discussed and it is concluded that, the coupling occurs so far in νC=O and νC=C takes on the character of out of phase and in phase modes respectively. In either conformer, the in phase νC=O mode gains the relative intensity as the frequency coverage, while s-cis conformer couple more, conjugation is unaffected by this, the true index of conjugation is neither νC=O nor νC=C, but mean frequency ν_m. The solvent effect appears to be related by the carbonyl, even a high polar C=C bond is insensitive to solvent unless otherwise stated (Fig.1).

Various compounds of non aromatic but highly conjugated molecules, most are basically amino ketones [1-4] though the phenomena of interest are confined by their spectroscopic characterization. They tend to be characterized by νC=C, νC=O and νN-H vibrations of quite exceptional intensity and some times at such low frequencies as to cost initial doubt on the assignment. Of these vibrations are more sensitive than carbonyl to bring changes in molecular structure (Fig.2).

Experimental

All the infrared spectra in 4000-400 cm^{-1} region were recorded using

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Perkin Elmer spectrophotometer. Solids were examined in as in Nujol mulls and in suitable solvents of spectroscopic grade (BDH).

5: *1-(o-chloro)-3-diphenyl propen-1-one*

Dioxane: 1725 st $\nu(C_6H_5\text{-}C)=O$ keto; 1665 st intramolecular H-bonding, 1510 w a-form, 1430 sm, b-form, 1325 sm C-C-C & C-CO-C bending; 1265 m, phenyl carbon str. bending 1210 sm c-form, 1175 in, 1 1,2-disubstituted aryl gr. 1105 sm, 1070 sm, 1065 m, 1030 m, 1,2-disubstituted aryl ring, 800 st δ(OH); 770 sm, (=C-H). 745 st, 710 m, (=CH) aryl out-of-plane def. and 630 sm, ring in-plane def.

6: *1-(o-chlorophenyl)-3-(o-hydroxyphenyl) propen-1-one*

Nujol: 1690 st $\nu(C_6H_5\text{-}C)=O$ keto; 1610 st C=CH aryl; 1580 m, C=C conjugated to C=O; 1455 st a-form; 1380 m b-form 1360 m, 1300 st, d-form; 1235 m e-form, 1225 $\nu C\text{-}COC_6H_5$; 1070 m and 1050 m, 1,2-disubstituted phenyl ring; 1030 m, 995 m, δ(OH), 945 m, 900 m, 840 m, 750 ν(=CH-); 700 st ring out-of-plane def. and 650 m, ring in-plane def.

7: *1-(m-nitro)-3-diphenyl propen-1-one*

Nujol: 1700 m, $\nu(C_6H_5\text{-}C)$; 1650 st, $\nu(C_6H_5\text{-}C)=O$ keto; 1610 sh α-hydroxy-keto; 1565 m a-form; 1515 sh, m b-form 1435 m, aromatic; 1380 st. c-form; 1340 m, 1300 st, 1260 sh, m d-form, 1240 m, e-form 1214 m $C\text{-}COC_6H_5$; 1170m, sh & =CH-C, 1150 m, $C\text{-}CO\text{-}C_6H_5$; 1030 m, 980 str. 760 str. ν(=CH-); 720 m, ring in-plane-def. 610 m, ring out-of-plane def.

Dichloromethane: 1690 m $\nu(C_6H_5\text{-}C)=O$ keto; 1630 str. ν(C=O) keto, 1610 α-hydroxy-diketone; 1590 m a-form; 1580 sm, 1520 sm, 1495 m, b-form, 1460 ν(CH=CH-), 1450 m aromatic, 1370 sm, c-form, 1650 sm, 1300, 1260 m, d-form, 1240 sm, e-form, 1210 sm, $(C\text{-}CO\text{-}C_6H_5)$ 1170 m, δ(=CH-); 1030 m, st, 980 st δ(OH), 870 m, 830 st; 850 st, 760 st divided ν(-CH) 660 m, ring out-of-plane def.

8: *1-(p-dimethylamino)-1,3-diphenyl propen-1-one*

Dichloromethane: 1710 st, $\nu(C_6H_5\text{-}C)=O$ keto; 1650 sm intramolecular H-bonding; 1530 sm a-form, 1470 sm, b-form; 1450 sm; 1390 (CH=CH) aryl gr. 1340 m, -C-C=C and -C=CO=C bonding; 1280 st, 1235 m c-form; 1220 sm, 1045 st, 1,4-disubstituted phenyl ring, 980 m, δ(OH), 945 m δ(OH), 880 st. and 880 st, for ν(CH=CH) out-of-plane def. 780 st. (=C-H); 675 m, (=C-H) aryl out-of-plane def. 660 m, C-CO-C aryl substituted in-plane def.

9: *1-(p-methoxyphenyl)-3-(hydroxyphenyl) propen-1-one*

Dioxane: 1710 st $\nu(C_6H_5\text{-}C)=O$ keto; 1645 sm ν(C=O) keto, 1610 vw ν(CH=CH), aryl; 1570 w a-form, 1515 st, 1490 m, b-form; 1370 sm, c-form; 1050

sm δ(-CO-C_6H_5); 880 w δ(OH), 830 m, out-of-plane def. 770 m ν(=CH-), 660 ring in-plane def., 620 m, ring out-of-plane def.

10: *1-(p-methoxy)1,3-diphenyl propen-1-one*

Nujol: 1700 m, st ν(C_6H_5-C)=O keto; 1640 m, intramolecular H-bonding 1585 sm νHC=CH conjugated to C=O, 1570 sm a-form; 1510 m, b-form 1460 st νHC=CH in phenyl ring; 1380 st, c-form, 1300 m, phenyl carbonyl str. C-C-C bending & C-CO-C bending; 1255 m, d-form; 1135 w and sm and 1030 1,2-disubst. benzene ring; 985 sm δ(OH), 820 m, (=CH-) out-of-plane def. 800 m, 760 m, and 720 (=C-H) aryl out-of-plane def. 660, 620, sm (C-CO-C) in-plane def.

Results and Discussion

The synthesis of unsymmetrical α,β-unsaturated ketones is achieved by the conventional method, i.e. by the condensation of aromatic aldehyde and ketone under basic conditions. The salient feature of such reaction is that when the aldehyde molecule has no α-hydrogen, since there is no competition from ketone. But when the aldehyde has an α-hydrogen, it is the α-carbon of the ketone that adds to the carbonyl group of the aldehyde or the other way around [2]. The reaction can be made regioselective by preparing the enol derivatives of the ketones separately [3] and then adding this to aldehyde which assure that the coupling take place on the desired site of an unsymmetrical ketone. The reaction with preformed enol derivative provide a way to control stereoselectivity of the aldol condensation [4]. The reaction creates two new chiral centers and in most cases, there are four stereoisomers (Fig.**3**).

Conformational effects in α,β-unsaturated diaryl ketones

The cis and trans conformational form present in the α,β-unsaturated ketones (Fig. **4**) have been elucidated by their infrared absorptions. The infrared spectral changes which account for, bringing the carbonyl function into conjugation with C=C double bond possesses special features have been explained satisfactorily. A typical data [5] of three generalized α,β-unsaturated ketones (**x,y,z**) have amply supported analysis. It has been concluded that a fall in frequency and rise in intensity on going from (**x**) to (**y**) form is by virtue of conjugation. However, a contradictory reasons have been given for the difference between (**y**) and (**z**) forms. Mecke and Noack [5] suggested that νC=O below and above 1600 cm^{-1} could be used to characterize α,β-unsaturated ketones as s-trans for (**y**) and s-cis for (**z**) forms respectively. They have interpreted the higher νC=O values in (**z**) form and as employing poor conjugation. Consistently, Hayes and Timmon [6] have shown that the solvent sensitivity of C=O is much greater for s-trans conformers. Nevertheless, the IR assignments procure that non polar s-cis compound tend to resemble s-trans form. Timmon et.al [7] and Erskine and Waigh [8] have done to an opposite conclusion. Noack and Jones [9] have discussed these contradictions in a

schematic way. In so for as the form (**b**) contribute than (**ii-b**) should be more important than (**i-b**), since the mutual polarization of the positive and negative charges (field effect) [6,7] should be greater by four times [8]. Hence, ignoring vibrational coupling and considering only the effect on conjugation, both frequencies should be lower, and both intensities higher in s-cis and s-trans form. When the nature of coupling is crucial to the arguments that follows.

In the resting state of pure vibrations, α,β-unsaturated ketones have a large carbonyl dipole and a small induced dipole of the C=C bond. The contribution of (**iii-a**) and (**iv-b**) forms help to lower both frequencies and raise both intensities (Fig.**5**). The former is more for C=O since this shows a net gain in electron density. The latter proportionately more for ε_A(C=C), since νC=C is induced from nothing, for example the values of **x** and **y** mentioned in Table 1. It is therefore concluded that since νC=O and νC=C are essentially strong and weak dipoles respectively, nearly all effect of solvent [7,10,11] which is higher in the former.

Table 1.

Infrared data in tetrachloromethane for ketones

		νC=O cm^{-1}	ε_A	νC=C cm^{-1}
Typical unconjugated	**x**	1718	1.0	1667
= s-trans	**y**	1675	1.17	1664
= s-cis	**z**	1693	0.82	1624

ε_A = relative intensity to the carbonyl of **x**

Other predictions that follow, entire difference between the conformer is due to coupling, not by conjugation, it becomes reasonable that as Junge [10], has remarked the sum of the νC=O and νC=C solvent shift is more or less independent of conformation, since increased conjugation should increase the overall solvent shift.

Cis and trans configuration

It has been found that the characteristic impaired differences between the s-cis and s-trans configuration in α,β-unsaturated ketones are due to the coupling between the νC=O and νC=C and this difference is probably marginal. The evidence comes from the near intensity of ν_m, despite the higher frequency separation in the s-cis form, and the sum of ε_A(C=O) and ε_A(C=C) are different, indicates that the s-trans conformer do not operate [6,7]. Therefore, it was established that so for the coupling occurs, νC=O and νC=C takes place on the

character of out-of-phase and in-phase modes respectively [10]. The frequency lowering brought about by conjugation in α,β-unsaturated ketones, is pronounced. The C=C absorption dropped further that νC=O, since νC=C bond can loose double bond character to two single bonds but C=O to only one. Three facts stand out when the conformers are compared. Firstly, the ν_m, is almost constant, which is visualized by characteristic difference in Δν. Secondly, the effect of carbocation is independent of conformation; νC=O and νC=C falls in chloroform by about 65-85 cm^{-1}, respectively. Thirdly, s-values are greater but reflect conformation as previously for s-trans and s-cis forms, they lie at 0.2-0.5 cm^{-1} for simple α,β-unsaturated ketones. This points out to a high degree of vibration coupling which is greater, in the s-cis form. As supporting evidence for coupling hypothesis. We may note that the sum of the solvent shift is again independent of the conformer.

The lower vibration in each pair is extra ordinarily intense by normal IR standard, and beyond all comparison stronger than anything previously reported for νC=C. To the extent that νC=C is really vs C=C/C=O then this comparison is misleading, and the sum of ε_A(C=O) and ε_A(C=C) should properly be compared. Nevertheless, the assignments at 1500-2000 cm^{-1} for simple enones as to indicate that they are to be the resonance hybrid.

Phenyl alkene stretching vibration (1600-1500 cm^{-1})

L. J. Bellamy [12] assigns the bands at 1565 cm^{-1} in benzalacetophenone to phenyl alkene stretching vibrations. The νC=C stretching vibration near 1600 cm^{-1} is observed when there is conjugation of νC=C to aromatic systems. The effect of conjugation of a double bond with a carbonyl group is ketone and assigned a frequency range of 1650-1620 cm^{-1}. The mono substituted phenyl ring with strong electron accepting or donating group, the band appears at 1625-1590 cm^{-1} of medium intensity. The second band at 1590-1575 cm^{-1} being weaker but indicating a weak interaction in groups.

The position of the phenyl alkene band is very sensitive to the substitution in the aromatic ring. An increase in conjugation in the system brings about a bathochromic shift in this band as expected. On introducing o-hydroxyl group in position eg. p-methoxybenzal-o-hydroxyacetophenone, thus νC=C shifts to 1632 cm^{-1} from 1640 cm^{-1}. The substitution in 2- and 4- position help the existence of resonance structures thereby shifting the VC=C stretching band to the lower frequency, whereas a substituent in m-position is not helpful in this respect. Thus the νC=C band in m-nitrobenzal acetophenone appears at 1632 cm^{-1}. For the m-substituted benzenes, intensity of the band at 1600 cm^{-1} is directly dependent on the sum of the electronic effect of the substituent whereas for p-substituted 1,4-positions phenyl group is dependent on the difference of the electronic effect of the substituent. For example, due to large dipole change possible for the p-substituted aryl compounds in which one group is o- p-

directing and the other is m- directing, then the band at 1625-1590 cm^{-1} is quite intense.

The band assignments at 1500-1400 cm^{-1} can not be misinterpreted as due to the olefinic C=C stretching vibration. Since the latter be out side the range. However, the band near 1450 cm^{-1} may be observed by the band due to the aliphatic =C-H deformation vibration.

-OCH_3 group absorptions (1300-1200 cm^{-1})

The methoxy group substituted to phenyl ring in compound (**9-10**) is shown to have correlated bands in the range 1310-1210 cm^{-1} and 1050-1010 cm^{-1} [13,14] the latter bands, however, are missed on account of their low intensity and also because this group lies in the absorption range as due to aromatic -CH inplane deformation vibrations. The methoxy group gives an intense peak at 1260 cm^{-1} as one can identify an aromatic carbon-oxygen stretching frequency (asym C-O-C str.). The νC-H deformation vibrations due to the methyl group and so could not be separated out from the latter.

In 1,3-diaryl propenones (**fig. 4, 5-10**), phenyl rings are associated with carbonyl functions, and a medium band at 1300-1230 cm^{-1}. The phenyl groups are substituted with electron donating groups like -OCH_3, -OH and Cl at 2- and 4- positions, while the electron withdrawing group -NO_2 in compound (**7**), these groups have pushed a medium intensity band occurring in a narrow frequency range of 1300-1280 cm^{-1}. It can therefore, be assigned to the phenyl-carbonyl stretching vibration $=C-C=C$ of aromatic ketones. This band appears at 1275 cm^{-1} in acetophenone, and moreover 1282 cm^{-1} in benzalacetophenone.

Richard et al. [15] associated a band in the range 1360-1330 cm^{-1} (medium) with (OH) deformation vibration of the phenolic character. In all cases of substituted 1,3-diaryl propenones with a phenolic group, two strong peaks at 1335±5 cm^{-1} and 1365-1350 cm^{-1} occurs.

Aromatic in-plane νCH deformation vibrations (1300-1000 cm^{-1})

A number of νCH in-plane deformation bands occurs in the region 1300-1000 cm^{-1}, these bands are found sharp, of weak to medium intensity. These bands are virtually not important for interpretation. The polar groups such as MeO, -$N(CH_3)_2$, OH and Cl have resulted in the intensity of these bands.

C-H out-of-plane deformation vibrations (1000-700 cm^{-1})

1,3-diaryl propenones (**Fig. 4, 5-10**) fall in the same range as for the substituted benzenes. In the case of 1,2-disubstituted phenyl rings almost all the spectra had shown two absorption peaks in the range of 740-640 cm^{-1}, attributing to four adjacent unsubstituted hydrogen atoms. The out-of-plane νC-H deformation vibration in the 1,3-disubstituted compounds due to three adjacent unsubstituted hydrogen atoms appear at 815±5 cm^{-1}. These νC-H out-of-plane

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deformation vibrations are determined by the number of adjacent atoms on ring and not very much affected by the nature of the substituent. Although strong electron withdrawing group, such as NO_2 results in an increase of 30 cm^{-1} in frequency to the vibrations. In the case of 1,4-disubstituted compound, a strong band due to two adjacent unsubstituted hydrogen atoms appears at 820 cm^{-1}. In almost all the cases, there appeared a band of weak-medium intensity in the peak assignment area 750-720 cm^{-1}.

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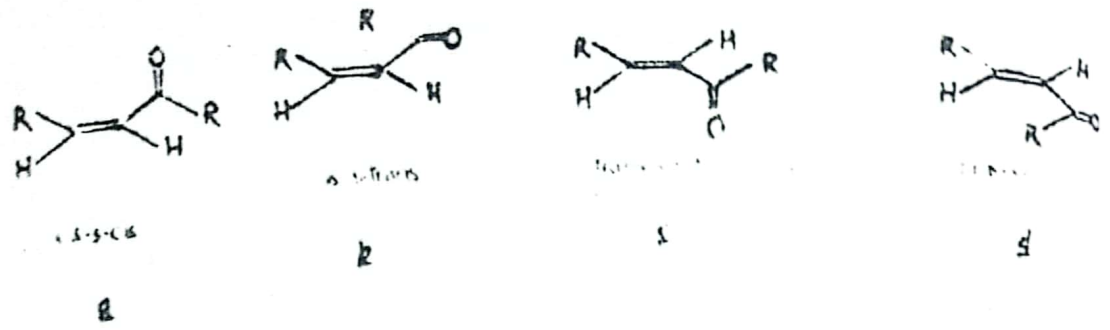


Fig. 1

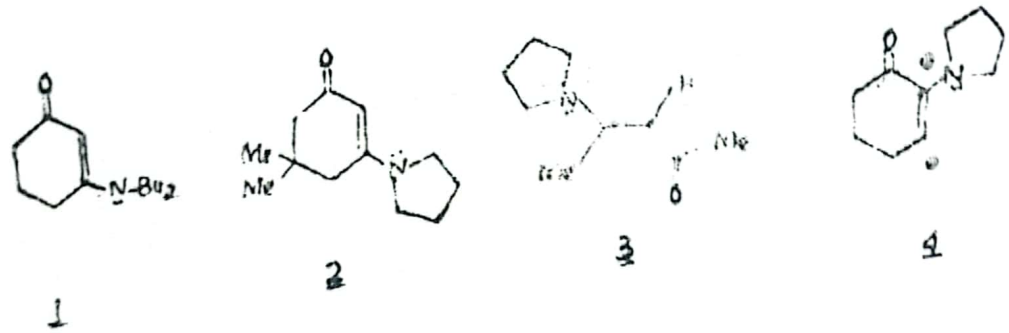


Fig. 2

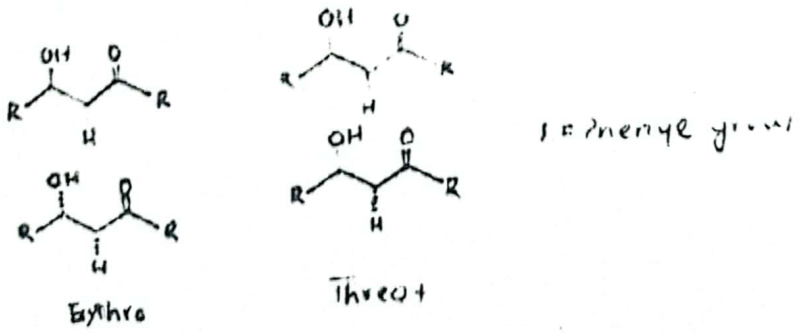
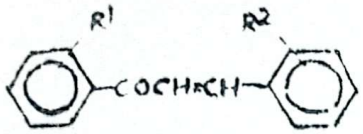


Fig. 3



5 $R^1 = Cl; R^2 = H$

6 $R^1 = Cl; R^2 = OH$

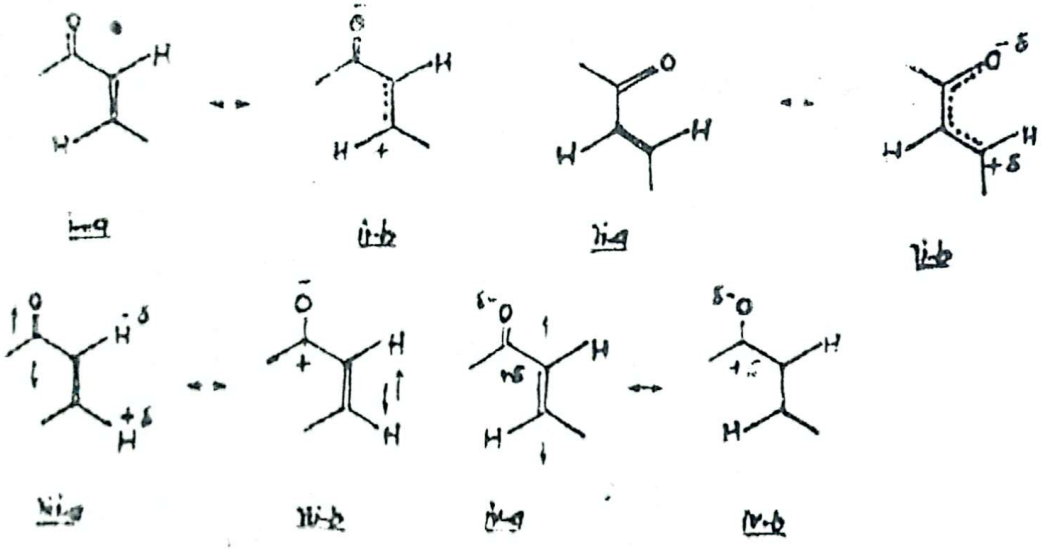
7 $R^1 = NO_2; R^2 = H$

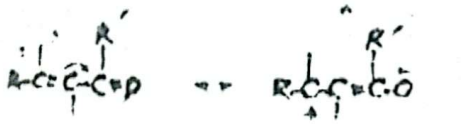
8 $R^1 = N(CH_3)_2; R^2 = H$

9 $R^1 = OCH_3; R^2 = OH$

10 $R^1 = OCH_3; R^2 = H$

Fig. 4





R and R′ = Alkyl or Aryl group

Fig. 5