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CONFORMATIONAL STUDY ON SOME β-PHENYL-α,β-UNSATURATED KETONES

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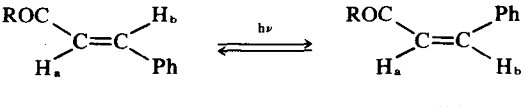
Abstract—The conformation of three (*E*)-β-phenyl-α,β-unsaturated ketones and their corresponding (*Z*)-isomers **1**, **2**, and **3** was established by IR and ASIS. (*Z*)-**1** and (*E*)-**1** have exclusively the *s-trans* conformation. The two isomers of **2** occur in both conformations but there is a higher *s-cis* to *s-trans* ratio with the (*Z*) than with the (*E*)-isomer. (*Z*)-**3** appears to exist exclusively in the *s-cis* conformation, the (*E*)-isomer has a small content of the *s-trans* conformation. It was concluded that the ASIS for H_b is a measure of the *s-cis* content of the conformational equilibrium.

During our study on the photoisomerization of α-keto oxime ethers it soon became apparent that the composition of the equilibrium mixture of the *s-trans* and *s-cis* conformers is dependent on the configuration around the double bond. In order to gain more insight into this question, a conformational investigation was undertaken of some related α,β-unsaturated ketones, viz. 3-phenylpropenal **1**, 4-phenyl-3-butenone **2**, and 1,3-diphenylpropenone **3**.

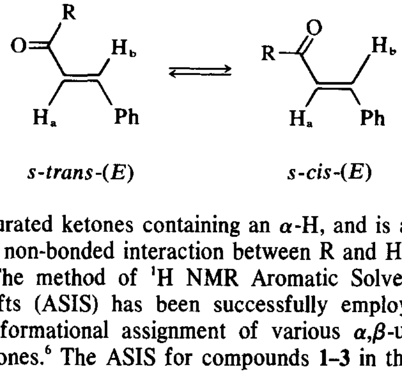
The three selected compounds all exist in the thermodynamically more stable (*E*)-configuration, as was concluded from the value of the ^{1}H NMR coupling constant $J_{a,b}$. The (*Z*)-isomers of **1–3** were readily obtained by irradiation of the (*E*)-isomers in benzene with λ 366 nm [equil. (1)] and preparative GLC separation.



(*E*) (*Z*) (1)

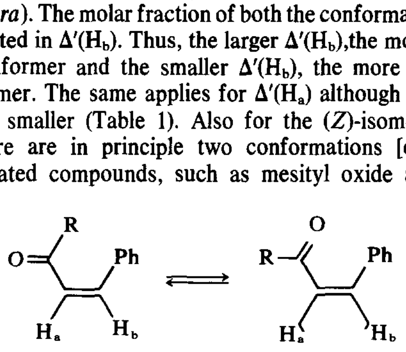
1: R = H$_c$
2: R = Me
3: R = Ph

Hayes and Timmons[1] have estimated the molar fraction x of the *s-trans* and *s-cis* conformers of some (*E*)-α,β-unsaturated ketones from the IR carbonyl absorptions, assuming that the specific intensities of the two conformers† ($i_{s\text{-}trans}$ and $i_{s\text{-}cis}$) are the same. However, from studies on molecules with fixed conformations[3,4] it appears that $i_{s\text{-}trans} > i_{s\text{-}cis}$. Following the method outlined by Bienvenüe[2] the molar fraction of the *s-trans*-(*E*) isomer in CCl_4 solution was calculated to be 1.0 (1.0) for **1**, 0.54 (0.71) for **2**, and 0.09 (0.16) for **3**, using $i_{s\text{-}trans} = 11300$ and $i_{s\text{-}cis} = 5400$ l. mole^{-1}. cm^{-1};‡ the data in parentheses are the ones reported by Hayes and Timmons. Accordingly, the molar fraction of the *s-cis* conformer becomes larger with increasing size of the group R [equil. (2)]. This tendency is well-established for α,β-unsaturated ketones containing an α-H, and is ascribed to the non-bonded interaction between R and H_b.[1,3,5]



s-trans-(*E*) *s-cis*-(*E*) (2)

The method of ^{1}H NMR Aromatic Solvent-Induced Shifts (ASIS) has been successfully employed in the conformational assignment of various α,β-unsaturated ketones.[6] The ASIS for compounds **1–3** in the (*E*)- and (*Z*)-configurations are collected in Table 1. On the basis of the differences of complexation of carbonyl containing compounds with $CDCl_3$ and C_6D_6,[6] it is to be expected [equil. (2)] that $\Delta'(H_b)$ will be very small (or even negative) for the *s-cis*-(*E*) conformation, and much larger for the *s-trans*-(*E*) conformation. From (*E*)-**1** to (*E*)-**3** there is a large decrease in $\Delta'(H_b)$ (Table 1). Compound (*E*)-**1** exists exclusively in the *s-trans* conformation and (*E*)-**3** almost exclusively in the *s-cis* conformation (*vide supra*). The molar fraction of both the conformations is reflected in $\Delta'(H_b)$. Thus, the larger $\Delta'(H_b)$, the more *s-trans* conformer and the smaller $\Delta'(H_b)$, the more *s-cis* conformer. The same applies for $\Delta'(H_a)$ although the values are smaller (Table 1). Also for the (*Z*)-isomers of **1–3** there are in principle two conformations [equil. (3)]. Related compounds, such as mesityl oxide and (*Z*)-3-pentenone have exclusively the *s-cis* conformation,[3,4,7–10] most probably as result of the strong steric constraint



s-trans-(*Z*) *s-cis*-(*Z*) (3)

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†The specific intensity i of a given conformer is defined by i = I/x, where I is the measured band intensity and x the molar fraction of this conformer.[2]

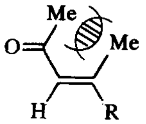
‡The specific intensities were calculated, using the data from Hayes and Timmons.[1]

Table 1. ^1H NMR and ASIS data (δ and Δ'†) for the (*E*)- and (*Z*)-isomers of **1**–**3**

Ketone	Solvent	H_b	H_a	$H_{aromatic}$	R	$J_{a,b}$	$J_{a,c}$
(*E*)-**1**	$CDCl_3$	7.47	6.71	7.64–7.33 (o, m, p)	9.71	16.1	7.6
	C_6D_6	6.81	6.46	7.20–6.98 (o, m, p)	9.46	16.0	7.1
	Δ'	0.66	0.25	0.4	0.25		
(*E*)-**2**	$CDCl_3$	7.50	6.71	7.57–7.31 (o, m, p)	2.36	16.2	
	C_6D_6	7.28	6.53	7.25–7.00 (o, m, p)	1.98	16.7	
	Δ'	0.22	0.18	0.3	0.38		
(*E*)-**3**	$CDCl_3$	7.78	7.44	7.69–7.32 (o, m, p)	8.07–7.92 (o) 7.69–7.32 (m, p)	16.4	
	C_6D_6	7.84	7.35	7.35–7.02 (o, m, p)	8.01–7.87 (o) 7.35–7.02 (m, p)	17.0	
	Δ'	−0.06	0.09	0.3	0.1 (o); 0.3 (m, p)		
(*Z*)-**1**	$CDCl_3$	7.62	6.20	7.60–7.30 (o, m, p)	10.00	11.5	8.0
	C_6D_6	6.89	5.93	7.07–6.87 (o, m, p)	9.88	11.9	8.0
	Δ'	0.73	0.27	0.5	0.12		
(*Z*)-**2**	$CDCl_3$	6.89	6.17	7.57–7.28 (o, m, p)	2.15	12.6	
	C_6D_6	6.44	5.84	7.49–7.35 (o) 7.21–7.00 (m, p)	1.81	12.7	
	Δ'	0.45	0.33	0.1 (o); 0.3 (m, p)	0.34		
(*Z*)-**3**	$CDCl_3$	7.02	6.63	7.63–7.18 (o, m, p)	8.04–7.92 (o) 7.63–7.18 (m, p)	13.0	
	C_6D_6	6.58	6.27	7.47–7.32 (o) 7.23–6.88 (m, p)	7.96–7.82 (o) 7.23–6.88 (m, p)	13.0	
	Δ'	0.44	0.36	0.0 (o); 0.4 (m, p)	0.1 (o); 0.4 (m, p)		

†$\Delta' = \delta_{CDCl_3} - \delta_{C_6D_6}$, all values in ppm; J in Hz.

between the two methyl groups in the *s-trans* conformation.



The decrease in $\Delta'(H_b)$ is substantially less on going from (*Z*)-**1** to (*Z*)-**3** than from (*E*)-**1** to (*E*)-**3** (Table 1). Characteristic for the *s-cis*-(*Z*) conformation is the substantial deshielding of the aromatic *ortho*-hydrogens with hexadeuterobenzene as solvent, as is apparent with (*Z*)-**2** and (*Z*)-**3**. Of course, such a specific deshielding of the *ortho*-hydrogens is not observed with the two conformations of the (*E*)-isomers. Also as a result of the anisotropy effect of the carbonyl group one may expect a deshielding of H_b for the *s-cis*-(*E*) conformation. The difference in chemical shift of the (*E*)- and (*Z*)-isomer of a given compound is listed in Table 2, together with the value for a related *s-cis* α,β-unsaturated ketone.[9]

The value of $\Delta\delta$ is just as $\Delta'(H_b)$ a measure for the relative content of the *s-cis* conformation in the conformational equilibrium (2): the more positive the value, the higher the content of *s-cis* conformer.

Table 2. Difference between the chemical shift of H_b of the (*E*)- and (*Z*)-isomer of α,β-unsaturated ketones

Compound	$\Delta\delta$ (ppm) CDCl$_3$	$\Delta\delta$ (ppm) C$_6$D$_6$
1	−0.15	−0.08
2	+0.61	+0.84
3	+0.76	+1.26
3-pentenone[8]	+0.62 (CCl_4)	

The main bands of the IR spectra in between 1600 and 1700 cm^{-1} of the compounds (*E*)-**1** to (*E*)-**3** and (*Z*)-**1** to (*Z*)-**3** are collected in Table 3. The assignments for the (*E*)-isomers are consonant with those of earlier investigations.[1,5,7] In the case of (*E*)-**1** and (*Z*)-**1** there are only two bands which are assigned to the *s-trans* conformation. On the contrary (*E*)-**2** gives rise to four bands which belong to both the conformations.‡ The IR spectrum of (*Z*)-**2** also shows four bands. The intensity of the *s-cis* C=O band is increased, whereas that of the *s-trans* C=C band is decreased, both relative to the corresponding absorptions of (*E*)-**2**. Compound (*E*)-**3** also shows two carbonyl bands of which that of the *s-cis* conformer is by far the strongest. In contrast, (*Z*)-**3** does not exhibit an *s-trans* C=O band, and apparently exists exclusively in the *s-cis* conformation.

In conclusion it has been shown by NMR and IR that three (*E*)-β-phenyl-α,β-unsaturated ketones (**1**–**3**) upon irradiation undergo facile (*E*)–(*Z*)-isomerization. In the (*Z*)-configuration ketone (*Z*)-**1** has exclusively the *s-trans* conformation. With compound **2** there is a higher

Table 3. IR frequencies ($CHCl_3$; cm^{-1}) of α,β-unsaturated ketones

	C=O		C=C	
Compound	*s-cis*	*s-trans*	*s-trans*	*s-cis*
(*E*)-**1**	—	1675 (s)	1630 (m)	—
-**2**	1688 (m)	1668 (s)	1638 (m)	1609 (s)
-**3**	1666 (s)	1640 (m)	—	1605 (s)
(*Z*)-**1**	—	1675 (s)	1616 (w)	—
-**2**	1690 (s)	1670 (s)	1622 (sh)	1607 (s)
-**3**	1665 (s) 1655 (sh)	—	—	1605 (sh) 1600 (s)

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‡The ratio of the band intensities of the C=O and the C=C stretching vibrations is considerably greater for the *s-trans* than the *s-cis* ketones.

s-cis to *s-trans* ratio with the (*Z*)- than with the (*E*)-isomer. Finally, compound (*Z*)-**3** appears to exist exclusively in the *s-cis* conformation; in contrast, the (*E*)-isomer has a small content of the *s-trans* conformation.

The observed variations in the ratios of the *s-cis* and *s-trans* conformations may be explained in terms of non-bonded interactions between the group R and the β-phenyl group in the *s-trans-(z)* conformation [equil. (3)], which increases in the order R = H, R = Me to R = Ph.

EXPERIMENTAL

Spectra. IR spectra were recorded on a Perkin Elmer 177 Grating Infrared Spectrophotometer. ^{1}H NMR spectra were obtained on a Varian HA-100 or XL-100 instrument with TMS as internal reference.

Materials. (*E*)-3-phenylpropenal was obtained from BDH. (*E*)-4-phenyl-3-butenone and (*E*)-1,3-diphenylpropenone were synthetized by condensation of benzaldehyde in basic solution with acetone and acetophenone respectively. The corresponding (*Z*)-isomers were prepared by irradiation of the (*E*)-isomers in benzene with λ 366 nm, and subsequent GLC separation of the resulting mixture on a copper column, 4 m, $\frac{1}{4}''$, 10%, Carbowax 20 M on Chromosorb W, 45–60 Mesh, using helium as carrier gas.

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