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Spectroscopic Study of Alkyl Vinyl Ketones

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Synopsis. Alkyl vinyl ketones have two conformations, *s-cis* and *s-trans*. The ratios of the two conformers are given by comparing their IR with NMR data. The conformer of *s-cis* is given by the equation, Percentage of *s-cis*$=180\cdot(\Delta\delta\ -0.15)$ (%), where $\Delta\delta$ is the chemical shift difference between *cis* and *trans* protons for carbonyl group. The value of ΔF obtained by means of the equation is related to steric factors Es^c of bearing alkyl groups. The ratio *s-cis/s-trans* is determined by the bulkiness of the alkyl group.

Alkyl vinyl ketones (AVK) are in equilibrium between two comparatively stable conformations, *s-cis* and *s-trans*. NMR spectra of AVK were studied and discussed as regards mono substituted ethylene.[1] Kossanyi[2] determined seven kinds of AVK in arbitrary units ($\delta\ cis+\delta trans+\delta gem=0$) and reported the effect of the alkyl group. The chemical shift of each vinylic proton can not be compared with other AVK, nor considered to be caused by conformation. The relation between conformations of β,β disubstituted enone and its chemical shift difference, reported by Cottee and Timmons,[3] and Faulk and Fry,[4] seems to be applicable to AVK.

NMR measurement of AVK (CH_2=CH-CO-R, R= Me, *n*-Pr, *i*-Pr, cyclo-Hex, *tert*-Bu and Ph) was carried out in carbon tetrachloride. The chemical shifts of vinylic protons are listed in Table 1. The chemical shift of *cis* proton is shifted to lower magnetic field with the decrease of Taft's σ^* value,[5] contrary to the tendency of *trans* proton. No different effects of alkyl substituent seem to be found for the protons. For 2 methylene cycloalkanones, Klose[6] and Kaiser and Hooper[7] showed a correlation between the chemical shift difference of two geminal olefinic protons and dihedral angle about central C–C bond from the diamagnetic anisotropy of carbonyl group. Similary, the chemical shifts of AVK are greatly affected by its carbonyl group. Since the ketones seem to consist of two comparatively stable conformers, the observed values are the mean values of *s-cis* and *s-trans*, and seem to be proportional to Taft's σ^* values. For the sake of clarification chemical shift differences ($\Delta\delta=\delta cis—\delta trans$) are compared with the proportion of $\varepsilon^{a}_{c=o\ s\text{-}cis}$, $(\varepsilon^{a}_{c=o\ s\text{-}cis}/(\varepsilon^{a}_{c=o\ s\text{-}cis}+\varepsilon^{a}_{c=o\ s\text{-}trans}))$ *s-trans* which does not indicate the exact proportion but suggests the part of *s-cis*, as shown Fig. 1. Linearity is found to hold. The conformer of *s-cis* in conjugated enone is given by means of the following equation,

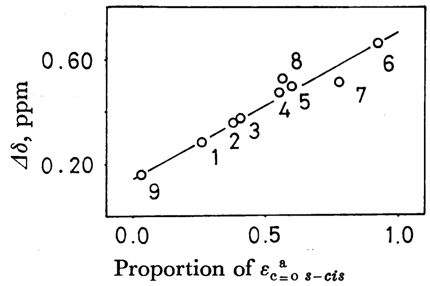

Fig. 1. Relation between the proportion of $\varepsilon_{c=o\ s\text{-}cis}$ and $\Delta\delta$.
(1=Me, 2=Et, 3=*n*-Pr, 4=cyclo-Hex, 5=*i*-Pr, 6=*t*-Bu, 7=Ph, 8=Methyl propenoate, 9=Propenal and 3-Methylbut-3-ene-2-one)

TABLE 1. NMR CHEMICAL SHIFTS OF VINYLIC PROTONS, RATIOS OF THEC=O s-*cis* TO C=O s-*trans* STRETCHING BAND ABSORBANCE AND Taft's σ^* VALUES OF BEARING ALKYL GROUP

Compound (R)	Chemical Shift (ppm)			Ratio of Absorbances	σ^*
	cis	*trans*	geminal		
1 Me	6.11	5.82	6.31	0.37	0.0
2 Et	6.12	5.76	6.35	0.61	−0.10
3 n-Pr	6.12	5.74	6.35	0.69	−0.115
4 iso-Pr	6.16	5.66	6.40	1.47	−0.19
5 cyclo-Hex	6.16	5.68	6.42	1.13	−0.15
6 tert-Bu	6.26	5.60	6.88	9.27	−0.30
7 Ph	6.35	5.83	7.09	4.17	0.60
8 H (Propenal)[a]	6.07	6.23	6.25	—	0.49
9 3-Methylbut-3-ene-2-one[b]	5.87	5.71	1.80 (CH_3)	0.03	
10 Methyl propenoate	0.533[c]			1.29[d]	

NMR spectra were measured in carbon tetrachloride (*ca.* 0.5 mol/l) with TMS at 35 °C, using Hitachi R-22 and Japan Electron Optics 4H-100. The chemical shifts were obtained from the spectra which were approximated to ABX type systems.

IR spectra were measured in carbon tetrachloride ($4.0—8.0\times10^{-2}$ mol/l) by the use of Shimadzu IR-27G type and NaCl and 0.2 mm spacer. Each AVK has C=O streching bands near 1700 cm^{-1}.

Higher frequency peak is assigned to *s-cis* the lower frequency peak to *s-trans* conformations.

a) Ref. 8, b) This value was given under the same condition as for the measurements of AVK. c) Ref. 10, d) This value gives the ratio of the C=C *s-cis* to C=C *s-trans* stretching band absorbance.[9]

Percentage of *s-cis*$=180(\Delta\delta-0.15)$ (%). Since propeophenone contains high diamagnetic aromatic group, $\Delta\delta$ of propeophenone deviates from linearity. The value of *s-trans* (0.15 ppm) agrees completely with that of 2-methylene cycloalkanones reported by Kaiser and Hooper,7) and that proposed for but-3-ene-2-one (R=Me) from carbonyl anisotropy by Barlet *et al.*11) However, $\Delta\delta$ of *s-cis* (0.72 ppm) appears higher than both the former value7) (0.64 ppm) and the latter value11) (0.63 ppm). Since calculated values of AVK by means of Pople's data12) are 0.79 ppm for *s-cis* and 0.19 ppm for *s-trans* (0.80 ppm and 0.12 ppm for but-3-ene-2-one, respectively),* $\Delta\delta$ of *s-cis* is acceptable. The results support the view that the relation is suitable for CH_2=C–C=O compounds, propenal,8)** methyl propenoate9,10) and 3 methyl but-3-ene-2-one, which have stable *s-cis* and *s-trans* but not effective shielding groups.

TABLE 2. K AND ΔF OF AVK BY EMPLOYING THE EQUATION

Compound R	$\Delta\delta$ (ppm)	*s-cis* (%)	K *s-cis/s-trans*	$\Delta F\times 10$a) (kcal/mol)	E_s^c
Me	0.29	25	0.34	6.63	0.0
Et	0.36	38	0.61	3.03	−0.38
n-Pr	0.38	41	0.71	2.12	−0.67
i-Pr	0.50	63	1.70	−3.23	−1.09
cyclo-Hex	0.48	59	1.46	−2.30	−1.40
tert-Bu	0.66	92	11.2	−14.73	−2.46
H (Propenal)	0.16	2	0.02	*ca.* 25	
3-Methylbut-3-ene-2-one	0.16	2	0.02	*ca.* 25	

a) $\Delta F=F_{s\text{-}cis}-F_{s\text{-}trans}$.

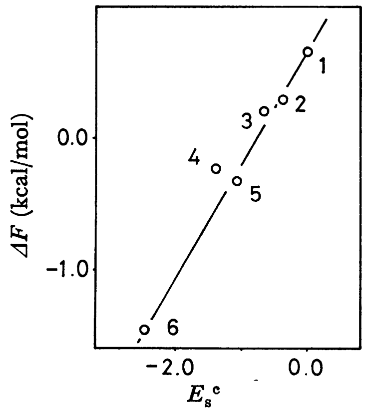

Fig. 2. Relation between ΔF and E_s^c (1=Me, 2=Et, 3=*N*-Pr, 4=cyclo-Hex, 5=*i*-Pr, 6=*t*-Bu)

The *s-cis*/*s-trans* ratio and free energy difference ($\Delta F=F_{s\text{-}cis}-F_{s\text{-}trans}$) are calculated by means of the ratio of *s-cis* (Table 2). Since ΔF seems to be affected by its alkyl groups, it is compared with Hancock's steric factor (Esc) which does not involve hyperconjugation term (Fig. 2). We see that a linear relation holds and that the *s-cis*/*s-trans* ratio of AVK is determined by the bulkiness of the bearing alkyl group.

Conclusion

The *s-cis*/*s-trans* ratio of AVK is determined by the bulkiness of the alkyl group. Its chemical shift difference of two geminal olefinic protons is determined by the ratio of conformers. ΔH and potential barrier of rotation can be roughly estimated by means of the relation between $\Delta\delta$ and *s-cis* percentage. The ΔH value of but-3-ene-2-one (R=Me) is determined by means of the change of temperature in NMR (0.34 kcal/mol). The result agrees with the value reported by Bowles *et al.*14) The change of the chemical shifts of vinylic protons are calculated for each conformations by the relation we obtained. Each chemical shift obtained is proportional to Taft's σ^* values of the bearing alkyl group.

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* The calculation was carried out using ideal molecular coordinates. ($r_{C=C}=1.34$ Å, $r_{=C-H}=1.08$ Å, $r_{=C-C=}=1.48$ Å, $r_{C=O}=1.21$ Å, $r_{C-CH_3}=1.54$ Å, $r_{C-H}=1.10$ Å (1.09 Å at position of carbonyl group), $\angle^{C}{}_{(SP^3)}=108°\ 28'$ $\angle^{C}{}_{(SP^2)}=120°$) $\chi_x^c=10.8$, $\chi_y^c=17.9$, $\chi_z^c=10.8$, $\chi_x^o=18.0$, $\chi_y^o=16.7$, $\chi_z^o=7.2$ on carbonyl group, $x^{C-C}=5.3$ paramagnetic term on C–C single bond. The value of x^{C-H} and x^{C-C} on C–C single bonds which are out of the conjugated plane are neglected.

** Courtieu *et al.*15) reported that propenal is *s-trans* form above 90% from NMR measurement. As $\nu_{c-o\ s\text{-}cis}$ could not be found, it is possible to consider that propenal is almost of s-*trans* conformation.