Tetrahedron Vol. 28, pp. 3449 to 3464. Pergamon Press 1972. Printed in Great Britain

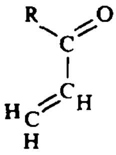
INFRARED INTENSITIES AS A QUANTITATIVE MEASURE OF INTRAMOLECULAR INTERACTIONS—XVIII[1]

ALKYL VINYL KETONES AND ALKYL PHENYL KETONES

A. R. KATRITZKY, R. F. PINZELLI and R. D. TOPSOM
School of Chemical Sciences, University of East Anglia, Norwich, England,
and School of Physical Sciences, La Trobe University, Melbourne, Australia.

(*Received in the UK* 10 *January* 1972; *Accepted for publication* 21 *March* 1972)

Abstract—The conformations of phenyl and vinyl alkyl ketones are discussed. The populations and individual integrated νC=C intensities are derived for s-*cis* and s-*trans* conformers of vinyl alkyl ketones and used to calculate total νC=C intensities which are in good agreement with those observed. Carbonyl intensities are also correlated with twist angles and are shown to have a similar dependence on molecular structure in the vinyl and aryl series.



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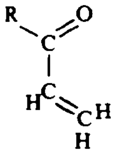
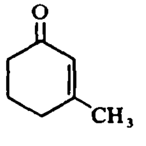


II

VINYL KETONES may exist in s-*trans*(I) and s-*cis*(II) conformations. Extensive studies of these compounds, and of models fixed in the s-*trans* or s-*cis* forms by ring formation, or otherwise, has shown that the IR and UV frequencies and intensities[2–7] and the NMR characteristics[8–11] vary according to conformation and this work has enabled recognition of the predominant conformers and the formulation of "rules" governing the variation of infrared intensities and frequencies of these compounds;[7] use has been made of model compounds, e.g. the spectral differences quoted[3] for III and IV are characteristic for the s-*trans* and s-*cis* configurations, respectively.[7] However, most



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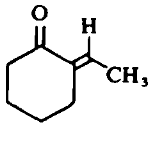
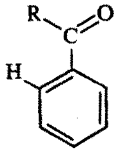


IV

of these studies have been qualitative, and none has treated the equilibria in terms of steric and electronic interaction energies. The present paper attempts such a quantitative treatment of the conformational equilibria I $\rightleftharpoons$ II for the compounds R = H through t-butyl.

Consideration of conformational equilibria for *αβ*-unsaturated ketones I $\rightleftharpoons$ II is complicated by the simultaneous occurrence of steric hindrance to planarity, of different mesomeric interactions in the s-*cis* and s-*trans* forms, and, possibly, of a different extent of vibrational coupling in the two conformers. We therefore initially studied phenyl ketones (V) as a model system in which variable steric hindrance to planarity occurred, but which only involves a single minimum energy value.



V

RESULTS AND DISCUSSION

Phenyl alkyl ketones; ring stretching intensities. From the experimental ν_{16} intensities listed in Table 1, we calculate σ_R° values for the acyl groups COR using Eq 1 which applies to monosubstituted benzenes.[14]

$$A_{\mathrm{mono}} = 17{,}600(\sigma_R^0)^2 + 100 \tag{1}$$

$$(\sigma_R^0)_{\mathrm{tw}} = (\sigma_R^0)_0 \cos^2 \phi \tag{2}$$

The considerable variation found in σ_R° (Table 2) for the COR groups with R = Me to R = $\mathrm{Bu^t}$ is, we believe, mainly a result of the equilibrium conformations of the acyl benzenes being such that the larger acyl groups are twisted out of the plane of the benzene ring. The effect of this twisting should be governed by a $\cos^2$ function as in Eq 2, where ϕ is the angle of twist and $(\sigma_R^\circ)_{\mathrm{tw}}$ the observed value whereas $(\sigma_R^\circ)_0$ would be that for a hypothetical COR coplanar with the benzene ring. We assume that the quantities $(\sigma_R^\circ)_0$ are closely similar for all COR groups (R = alkyl) but possibly different for CHO as discussed below.

Before discussing these σ_R° values in detail, it is useful to look at independent evidence concerning the rotational barriers in acyl benzenes. The measured barrier for benzaldehyde[15] is 7·9 kcal mole^{-1} and although barriers for rotation of the RCO group are not directly available, we can estimate that for the CH_3CO group in acetophenone. Thus the rotational barriers for *p*-methoxy-[15] (9·2 kcal mole^{-1}) and *p*-dimethylamino-benzaldehyde[15] (10·8 kcal mole^{-1}) and those for *p*-methoxy-[16] (7·3 kcal mole^{-1}) and *p*-dimethylamino-acetophenone[16] (8·5 kcal mole^{-1}) will be higher than the barriers in benzaldehyde and acetophenone themselves because of increased conjugation. This increased conjugation is greater in benzaldehydes with *p*-donor substituents than for the corresponding *p*-substituted acetophenones,[17] in the ratio of *ca* 4:3. The measured barrier for benzaldehyde given above is 7·9

TABLE 1. IR AND UV SPECTRA OF MONOSUBSTITUTED BENZENES

Subst.	ν_{16a}		ν_{16b}		$A\nu_{16}$[a]	$C{=}O$			UV lit		UV[c]	
	ν cm^{-1}	ε_a	ν cm^{-1}	ε_a		ν cm^{-1}	ε_a	A[a]	λ_{max}[b]	ε	λ_{max}[b]	ε
CHO	1598	80	1586	70	1150[d]	1707[d]	800	8050[d]	242[e]	14,000[e]	—	14,300[f]
COMe	1601	80	1581	40	940[d]	1692[d]	610	7300[d]	242[e]	13,200[e]	242	12,830
COEt	1598	50	1584	40	850	1692	380	6700	242[e] 237[g]	13,500[e] 11,450[g]	241	12,560
$COPr^i$	1596	60	1578	40	760[d]	1684[d]	370	6300[d]	238[g]	11,500[g]	242	12,050
COPh	1602	110	1580	60	750[d]	1662[d]	570	7600[d]	—	—	—	—
$COBu^t$	1599	30	1579	20	515	1674	320	6020	242[e]	9100[e]	239	8970
$COCMe_2Et$	1597	28	1574	15	500	1675	240	5900	239[e]	8300[e]	239	8840
$COCMeEt_2$	1597	28	1578	14	460	1675	290	5800	238[e]	7100[e]	239	7520
CH_2COH	1603[h]	18[h]	1587[h]	7[h]	314[h]	1726	330	6770	—	—	—	—
CH_2COMe	1602	20	1583	8	360	1717[i]	250	5840[i]	—	—	—	—

[a] Compounds in CCl_4 soln

[b] Value in nm

[c] Present work; solvent: abs. EtOH

[d] Compare work by G. Guiheneuf, C. Laurence and B. Wojtkowiak, *Bull. Soc. Chim. Fr.* 571 (1970): for ten integrated intensities values ($A\nu_{16}$ and A_{CO}) including $A\nu_{16}$ for chlorobenzene and ethoxybenzene the correlation is: $A_{obs} = 0{\cdot}932/2{\cdot}302.\ A_{lit.}\ 10^4$ ($r = 0{\cdot}9988$)

[e] Ref 12

[f] Value calculated. See footnote *f*, Table 2

[g] Ref 13.

[h] Ref 14

[i] Ref 3

kcal mole^{-1} and hence we can estimate the barrier for acetophenone as *ca* 6·4 kcal mole^{-1}, a difference of 1·5 kcal mole^{-1}.* In confirmation of this, the $\Delta H°$ difference between the s-*cis* and s-*trans* conformers of acraldehyde is 2·0 kcal mole^{-1} from microwave spectroscopy[18] (gas phase) and 2·0 kcal mole^{-1} from ultrasonic relaxation[19] (pure liquid) and that for methyl vinyl ketone is 0·5 kcal mole^{-1} from an IR intensity variation with temperature[20] (in CS_2 solution). In both cases the s-*trans* form is more stable.† The variation in the energy difference between the s-*cis* and s-*trans* forms of acraldehyde and methyl vinyl ketone arises at least in part from steric hindrance in the s-*trans* form of methyl vinyl ketone. The steric hindrance in s-*trans* methyl vinyl ketone compared to s-*trans* acraldehyde should be similar to the increased energy of the ground state of acetophenone relative to benzaldehyde (of structures I and II) and indeed is found to be identical to our estimate of 1·5 kcal mole^{-1}.

We can use this value of 1·5 kcal mole^{-1} to calculate the angle of twist in acetophenone taking the CHO group in benzaldehyde as coplanar with the ring and assuming that the energy difference arises entirely from steric causes. Thus we would have ϕ given by $6{\cdot}4 = 7{\cdot}9 \cos^2 \phi$ and derive a value of 25·70°. The $\cos^2$ form of barrier is supported by our unpublished calculations[21] and by the work of Meyer[22]

$$E_{ev} = 0{\cdot}65\, f(\phi) + 3{\cdot}65 \tag{3}$$

who calculated the energy of $n \rightarrow \pi^*$ transitions in twisted "phenyl carbonyl", C_6H_5CO, as a function of the overlap integral and hence of the angle of twist ϕ. His published results may be described by Eq 3 which requires that the function of ϕ be zero for a 90° twist out of plane and unity for 0° twist. The results in Table 3 show clearly that his results are well reproduced when $f(\phi)$ is taken as $\cos^2 \phi$.

We now return to the σ_R° values obtained (Table 2) from our measured intensities. If we follow the assumptions above that the CHO group is coplanar with the benzene ring and that the differences in σ_R° values measured reflect twisting out of the plane for the COR groups in acetophenone etc. then we can use Eq 4a to calculate the angle of twist. These assumptions are designated (a) throughout the paper and also in the relevant equations. Values of ϕ so obtained are shown in column 3 in Table 2. It is seen that the value of 18·4° for acetophenone is not too far different to that estimated above. However, such angles of twist seem rather large and they are derived on the assumption that the difference in conjugative powers of the COMe and CHO

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* In the gas phase, the energy barriers for benzaldehyde and acetophenone are quoted as 4·66 and 3·1 kcal mole^{-1}, respectively. *cf* F. A. Miller, W. G. Fately and R. E. Witkowski, *Spectrochim. Acta* **23A**, 891 (1967)

† Other work supports these conclusions, at least qualitatively. Thus acraldehyde has been shown to exist predominantly in the s-*trans* configuration (I) in solution from dipole moments [see Ref. 18 and J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.* 2957 (1949)]. The absence of any change of the IR spectrum of acraldehyde with temperature both in solution and in the vapour phase has also been interpreted[20] in terms of a large predominance of the s-*trans* form. Dipole moment measurements suggest that methyl vinyl ketone exists predominantly in the s-*trans* conformation [see [(a)] M. T. Rogers, *J. Am. Chem. Soc.* **69**, 2544 (1947); [(b)] P. D. Foster, V. M. Rao and R. F. Curl, Jr., *J. Chem. Phys.* **43**, 1064 (1965)] and this conclusion is supported by the microwave spectrum [see Ref *b* above].

TABLE 2. TWISTING IN ACYL BENZENES: ESTIMATION FROM IR AND UV DATA

1 Subst.	1 σ°_{R}[a]	2 σ°_{R}[b]	3 ϕ[d]	4 ϕ[e]	5 ϕ[f]	6 ϕ[g]	7 Z[h]	8 Z[i]	9 $\Delta G^{\ddagger}$[j]	10 $\Delta G^{\ddagger}$[k]
CHO	0·244	0·30	0	0	0	0	0	0	7·9	7·9
COMe	0·219	0·22	18° 44′	0	18° 40′	0	0·9	1·5	7·0	6·4
COEt	0·206	0·21	23° 14′	14° 6′	20° 25′	8° 21′	1·3	1·9	6·6	6·0
COPr^i	0·194	—	26° 55′	19° 45′	23° 23′	14° 17′	1·7	2·2	6·2	5·7
COPh	—	0·17[c]	33° 25′	28° 14′	—	—	2·4	2·9	5·5	5·0
COBu^t	0·154	0·12	37° 24′	33°	37° 37′	33° 13′	2·9	3·4	5·0	4·5
COCMe$_2$Et	0·150	—	38° 22′	34° 9′	38° 10′	33° 54′	3·1	3·5	4·8	4·4
COCMeEt$_2$	0·143	—	40° 3′	36° 6′	43° 31′	40° 3′	3·3	3·7	4·6	4·2

[a] Values calculated using Eq 1

[b] Value from ^{19}F NMR study. Private communication R. W. Taft

[c] Value from ^{19}F NMR study. Private communication R. W. Taft and W. A. Sheppard

[d] $\cos^2 \phi = (\sigma^{\circ}_{R})$COR/0·244

[e] $\cos^2 \phi = (\sigma^{\circ}_{R})$COR/0·219 (COMe)

[f] $\cos^2 \phi = \varepsilon/14{,}300$

[g] $\cos^2 \phi = \varepsilon/12{,}830$

[h] Kcal mole^{-1}, from Eq 7a

[i] Kcal mole^{-1}, from Eq 7b

[j] $\Delta G^{\ddagger} = 7·9 \cos^2 \phi$, with $\cos^2 \phi$ from Eq 4a

[k] $\Delta G^{\ddagger} = 6·4 \cos^2 \phi$, with $\cos^2 \phi$ from Eq 4b

TABLE 3. CALCULATION OF $f(\phi)$ USING EQUATION (3)

ϕ	10°	20°	30°	40°	50°	60°	70°
$E_{ev}{}^{a}$	4·27	4·2	4·125	4·0	3·725	3·8	3·9
$f(\phi)$	0·95	0·85	0·73	0·54	0·39	0·23	0·12
$\cos^2 \phi$	0·97	0·83	0·75	0·59	0·41	0·25	0·12

[a] Ref 22

is *solely* a consequence of steric hindrance. Therefore we also have carried out calculations on the alternative extreme assumption that acetophenone is planar and that the difference in conjugative powers of COMe and CHO is *solely* a consequence of different electronic effects.

$$\sigma^{\circ}_{R\,(COR)} = \sigma^{\circ}_{R\,(CHO)} \cos^2 \phi \tag{4a}$$

This alternative is designated (b) throughout the paper and in the relevant equations. The angle of twist for the alkyl phenyl ketones is here derived from Eq 4b, (values shown in column 4 in Table 2). The true situation presumably lies between these extremes. Unfortunately, suitable X-ray or electron diffraction data are apparently not available to compare with the predicted angles[23] although our σ°_{R} (COR) values are linearly related to the $^{13}C_{(CO)}$ chemical shift[24] of benzaldehyde and alkyl phenyl ketones. Fortunately, as will be shown, the relations deduced are essentially

$$\sigma^{\circ}_{R\,(COR)} = \sigma^{\circ}_{R\,(COMe)} \cos^2 \phi \tag{4b}$$

similar for the two sets of assumptions (a) and (b).[21] Another assumption implicit in Eq 4 is that no resonance interaction occurs between a COR group and an orthogonal benzene ring: this is reasonable in view of the very low σ°_{R} values for groups such as $CHCl_2$.[14]

$$(\sigma^{\circ}_{R})_0 = 0{\cdot}219/\cos^2 25{\cdot}70 = 0{\cdot}270 \tag{5a}$$

Values of ϕ have been obtained for the other RCO groups [(Table 2, Eq 4a col 3 and Eq 4b col 4)]. For treatment (a), the value of $(\sigma^{\circ}_{R})_0$ was derived from Eq 5a which is fairly close to the σ°_{R} value for CHO. In our subsequent development of treatment (a) we use the $(\sigma^{\circ}_{R})_0$, derived from Eq 5a except for PhCO. In PhCOPh the two rings are nonequivalent and we therefore use for both treatments (a) and (b) the σ°_{R} from ^{19}F NMR studies; this usage is justified later.

$$\cos^2 18°40' = 12830/\varepsilon_0 \tag{6a}$$

Table 2 also contains twist angles derived from UV data. Braude and Sondheimer originally used $\cos^2 \phi = \varepsilon/\varepsilon_0$, taking ε_{COMe} as ε_0, *i.e.* implicitly assuming coplanarity in acetophenone itself. We have, following treatment (b), calculated twist angles ϕ on this basis (see Table 2 col 6), using redetermined UV data. We have also [treatment (a)] taken ε_0 as 14300 derived from Eq 6a (*cf* $\varepsilon_0 = 14000$ for benzaldehyde value), where the possible nonplanarity of acetophenone is allowed for, and the resulting twist angles ϕ are given in col. 5 of Table 2. There is satisfactory agreement both between the values of ϕ in cols 3 and 5 and between those in cols 4 and 6 of Table 2. The energy increments, Z, of the ground states of the various acyl benzenes over

$$Z = 7{\cdot}9 - 7{\cdot}9\cos^2\phi \tag{7a}$$

$$Z = 7{\cdot}9 - 6{\cdot}4\cos^2\phi \tag{7b}$$

those of the hypothetical planar and fully conjugated molecule, calculated from Eqs 7a and 7b, which follow from the rotational energy barriers previously mentioned, according to treatments (a) and (b) are given in cols 7 and 8 of Table 2 and shown diagrammatically in Fig 1.

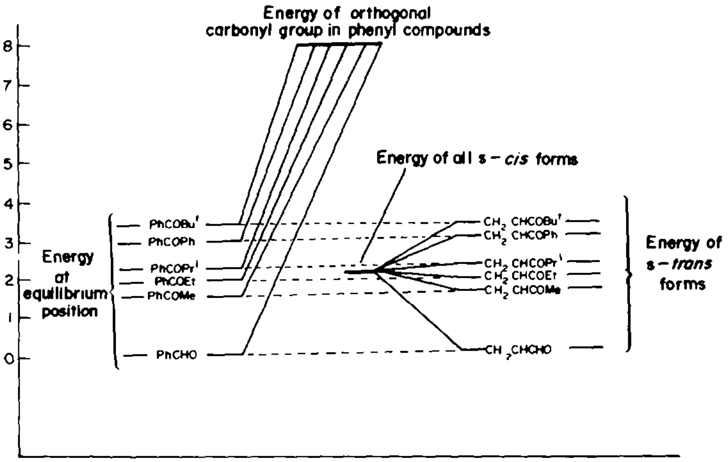


FIG. 1. Energy levels for s-*trans* and s-*cis* alkyl vinyl ketones and alkyl phenyl ketones (The values correspond to the treatment (b)—see text)

Phenyl alkyl ketones: carbonyl intensities. The intensities of the $\nu C{=}O$ group for phenyl alkyl ketones show (Table 1) a significant decrease as steric hindrance increases; for the tertiary alkyl groups they are near the values for $PhCH_2COMe$. The quantitative interpretation of this variation requires consideration of two superimposed effects: that intrinsic to the alkyl group and that caused by twisting of the acyl group out of the benzene ring plane. We estimate the first effect from the $\nu C{=}O$ intensities of alkyl methyl ketones (Table 4). The effect of twisting is therefore given by $\Delta A^{\ddagger}_{C=O}$ (Ph-Me)COR as defined by Eq 8, which should be proportional to $(\sigma_R^\circ)_{tw}$. The linear relation of Eq 9 is obeyed with $r = 0{\cdot}966$; values are compared in Table 4. Eq 10 then follows from Eqs 8 and 9. From Eq 9 $\Delta A^{\ddagger}_{C=O}$ (Ph-Me)COR should also be a linear function of $A^{\ddagger}_{mono}$: it is, with a slope close to unity (Fig 2) which may be significant.

$$\Delta A^{\ddagger}_{C=O}(\text{Ph-Me})\text{COR} = A^{\ddagger}_{C=O}(\text{PhCOR}) - A^{\ddagger}_{C=O}(\text{MeCOR}) \tag{8}$$

$$\Delta A^{\ddagger}_{C=O}(\text{Ph-Me})\text{COR} = 128(\sigma_R^\circ)_{tw} - 17 \qquad (9$$

$$A_{C=O}(\text{PhCOR}) = [A^{\ddagger}_{C=O}(\text{MeCOR}) + 128(\sigma_R^\circ)_{tw} - 17]^2 \tag{10}$$

$$A^{\ddagger}_{C=O}(\text{Ph-Me})\text{COR} = A^{\ddagger}_{C=O}(\text{PhCOPh}) - A^{\ddagger}_{C=O}(\text{MeCO mesit}) = 4.7 \tag{11}$$

For diphenyl ketone, both of the benzene rings are twisted significantly out of the C=O plane, but to differing extents. We may compare the effect of the less conjugated aryl group on the orientation of the conjugated aryl in PhCOPh by comparing PhCOPh with acetylmesitylene (VI); the value of 4·7 thus obtained

TABLE 4. ALKYL METHYL AND ALKYL PHENYL KETONES: FREQUENCIES AND IR INTENSITIES OF CARBONYL BANDS

R	MeCOR					PhCOR	(Ph-Me)COR	
	$\nu_{C=O}$ (cm^{-1})		$A_{C=O}$		$A^{\frac{1}{2}}_{C=O}$	$A^{\frac{1}{2}}_{C=O}$[c]	$A^{\frac{1}{2}}_{C=O}$	
	a	b	a	b	b		d	e
Me	1718	1716	5450	5360	73·2	85·4	12·2	11·0
Et	1722	1720	5240	5320	72·9	81·8	8·9	9·3
Pr^i	1719	1716	5900	5260	72·5	79·3	6·9	7·8
f	1705	—	6800	—	82·5	87·2[g]	4·7	5·1
Bu^t	1711	1708	5750	5520	74·3	77·6	3·3	3·0

[a] Ref 3
[b] Present work
[c] From Table 1
[d] Observed: see Eq 8
[e] Calculated: see Eq 9
[f] Mesityl
[g] With R = Ph

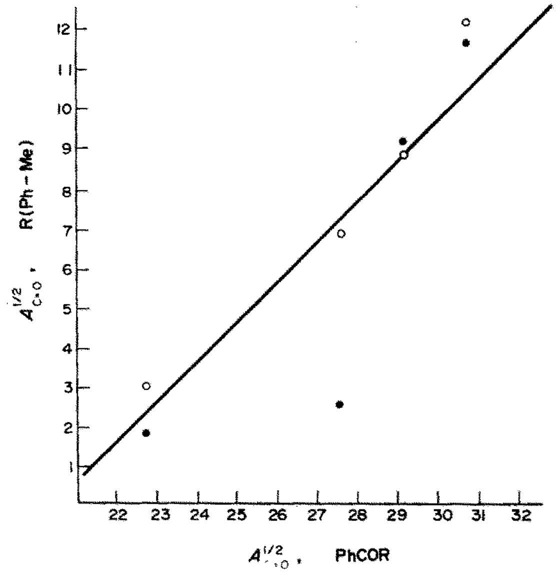
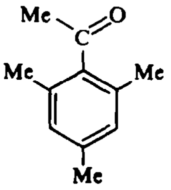
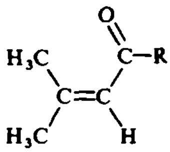


FIG. 2. Plots $\Delta A^{\frac{1}{2}}_{C=O\,R(Ph\text{-}Me)}$ against $A^{\frac{1}{2}}_{C=O\,PhCOR}$: ○, using $A^{\frac{1}{2}}_{C=O\,(MeCOR)}$ from present work; , ● using $A^{\frac{1}{2}}_{C=O\,(MeCOR)}$ from Ref. 3.

(Eq 11), is close to that of 5·1 found using the ^{19}F values of $\sigma_R^\circ = 0{\cdot}17$ for PhCO in Eq 9; this provides a justification for the use of this σ_R° value. X-Ray analysis of 3,3'-dibromobenzophenone gives an angle of twist of 22·4°; calculated values of ϕ are 33° (Eq 4a) or 28° (Eq 4b).



VI



VII

Vinyl ketones: conformational mole fractions. Vinyl ketones exist as equilibrium mixtures of s-*trans* (I) and s-*cis* (II) forms. If the mole fractions at equilibrium of forms I and II are α and $(1 - \alpha)$, we estimate α as follows. We assume no steric hindrance in the s-*cis* forms. In support of this assumption, compounds of type VII show $A_{C=C}$ and $A_{C=O}$, as well as ε_{max} (237 nm), which vary little for R = Me, Et, Pr^i, Bu^t; all the members of this series of compounds evidently exist in an unstrained s-*cis* form as shown (VII),[3–5] and there appears to be little steric hindrance for an alkyl group in the s-*cis* conformation.

For the s-*trans* form of a vinyl alkyl ketone the steric hindrance is equated to that in the corresponding phenyl alkyl ketone (cf I and III). The s-*cis* ⇌ s-*trans* energy differences are known to favour the s-*trans* form by 0·5 kcal mole^{-1} for methyl vinyl ketone and 2·0 kcal mole^{-1} for acraldehyde. The different energy increments, 2·0 and 0·5 for acraldehyde and methyl vinyl ketone, are considered in treatment (a) as due to steric hindrance, and in treatment (b) as caused by extra stabilization of the s-*trans* form of acraldehyde by a stronger resonance effect (*cf* PhCOR). We determine the corresponding ΔG° values (Table 2; cols 10 and 11) for the other ketones from the energy increments Z using Eqs 12a and 12b and fix the s-*trans* and s-*cis* energy levels as shown in Fig 1. The mole fractions α for the s-*trans* form follow

$$\Delta G_{s\text{-}cis/s\text{-}trans} = 2{\cdot}0 - x = 5{\cdot}9\text{–}7{\cdot}9\cos^2\phi \tag{12a}$$

$$\Delta G_{s\text{-}cis/s\text{-}trans} = 2{\cdot}0 - x = 5{\cdot}9\text{–}6{\cdot}4\cos^2\phi \tag{12b}$$

$$\frac{1-\alpha}{\alpha} = K = \exp\left(\frac{-\Delta G^\circ}{\mathrm{RT}}\right) = \exp\left(\frac{5{\cdot}9\text{–}7{\cdot}9\cos^2\phi}{\mathrm{RT}}\right) \tag{13a}$$

$$\frac{1-\alpha}{\alpha} = K = \exp\left(\frac{-\Delta G^\circ}{\mathrm{RT}}\right) = \exp\left(\frac{5{\cdot}9\text{–}6{\cdot}4\cos^2\phi}{\mathrm{RT}}\right) \tag{13b}$$

$$A_{C=C} = \alpha A_{s\text{-}trans} + (1-\alpha)A_{s\text{-}cis} \tag{14}$$

$$A_{s\text{-}trans} = \mathrm{a}[(\sigma_R^\circ)_{tw}]^2 = \mathrm{a}[(\sigma_R^\circ)_0]^2\cos^4\phi \tag{15}$$

$$A_{C=C} = \alpha\,.\,\mathrm{b}\,.\cos^4\phi + (1-\alpha)\mathrm{c} \tag{16}$$

$$A_{C=C} = \alpha\,.\,190\cos^4\phi + (1-\alpha)\,1800 \tag{17}$$

TABLE 5: VINYL ALKYL KETONES: C═C BANDS

R	a		b		α_{lit}[c]	ν cm^{-1}		ε_A		$A_{C=C}$			
	$\Delta G^{s\text{-}cis}_{s\text{-}trans}$	α	$\Delta G^{s\text{-}cis}_{s\text{-}trans}$	α		lit	obsd.	lit.	obsd.	lit	obsd.	calcd.[g]	calcd.[h]
H	+2·0	0·97	+2·0	0·97	1·00	1620[d]	1618	—	9	190[d]	180	240	240
Me	+1·1	0·86	+0·5	0·70	0·71	1618[d]	1618	~90[f]	50	690[d]	670	380	670
Et	+0·7	0·76	+0·1	0·53	0·61	1619[d]	1620	66[e]	59	1240[d]	950	535	935
Pr^i	+0·2	0·58	−0·3	0·38	0·43	1613[e]	1612	110[e]	95	—	1210	825	1170
Ph	−0·5	0·30	−1·0	0·16	0·16	1611[e]	1610	174[e]	107	—	1610	1290	1530
Bu^t	−1·0	0·16	−1·5	0·07	0·00	1610[e]	1609	146[e]	148	—	1720	1520	1680

[a] $\Delta G^{s\text{-}cis}_{s\text{-}trans}$; in kcal mole^{-1} from Eq 12a; α values from Eq 13a

[b] $\Delta G^{s\text{-}cis}_{s\text{-}trans}$; in kcal mole^{-1} from Eq 12b; α values from Eq 13b

[c] α values from literature study of styryl ketones, see W. P. Hayes and C. J. Timmons, *Spectrochim. Acta* **24A**, 323 (1968)

[d] From Ref 3

[e] From Ref 9

[f] See W. H. T. Davison and G. R. Bates, *J. Chem. Soc.* 2607 (1953).

[g] Using Eq 17, with α from Eq 13a and ϕ from Eq 4a

[h] Using Eq 17, with α from Eq 13b and ϕ from Eq 4b

from Eqs 13a and 13b and are listed in Table 5. The values $\alpha = 0{\cdot}16$ and $0{\cdot}07$ for the t-butyl compound are consistent with previous evidence; the appearance of only one resolved νC═O band suggests that this compound exists predominantly in the s-*cis* form.

Vinyl ketones: νC═C intensities. The measured IR intensity area for the νC═C band of an alkyl vinyl ketone will be the sum of the absorption of the individual s-*cis* and s-*trans* forms (Eq 14). If steric hindrance is absent in the s-*cis* form, $A_{s\text{-}cis}$ should be invarient with the alkyl group R. However, $A_{s\text{-}trans}$ is expected to vary with R in the manner of Eq 15, which is of the same form as Eq 1, because we have previously shown that the νC═C intensity for monosubstituted ethylenes is related to σ_R° by a relation similar to Eq 1.[25] Writing $A_{s\text{-}cis} = \text{c}$, and a. $[(\sigma_R^\circ)]^2 = \text{b}$, we can combine Eqs 14 and 15 to give Eq 16, where "b" and "c" are constants. We have six equations of type 16 for the νC═C intensities of the alkyl vinyl ketones CH_2:CHCOR with R = H, Me, Et, Pr^i, Ph, and Bu^t in which the only unknowns are "b" and "c". By a successive approximations technique, the six equations were fitted to find the best values: b = 190, c = 1800. Eq 17 follows. Values of $A_{C=C}$ calculated using Eq 17 are in satisfactory agreement with observed $A_{C=C}$ (Table 5) (correlation coefficient 0·990).

$$f(y) = \frac{y^2\,190}{1 + \exp[(5{\cdot}9 - 6{\cdot}4y)/0{\cdot}6]} + 1800\left\{1 - \frac{1}{1 + \exp[(5{\cdot}9 - 6{\cdot}4y)/0{\cdot}6]}\right\} \qquad (18b)$$

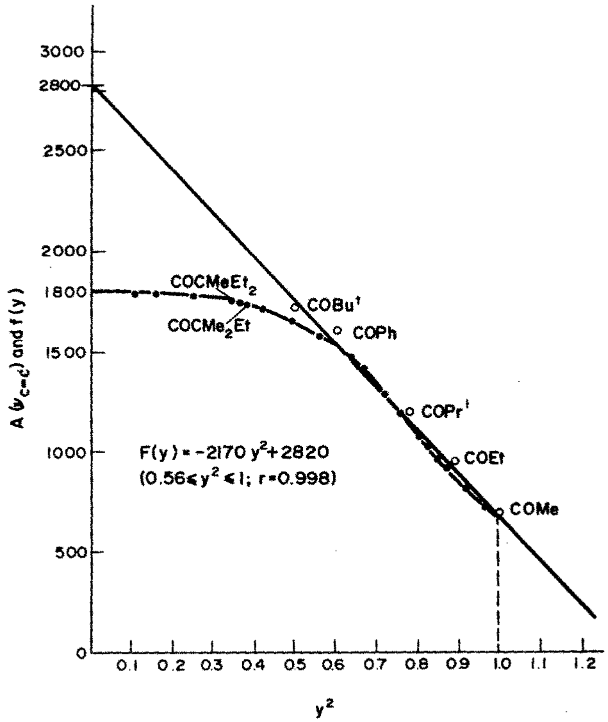


FIG. 3. ●, Plot of f(y) of Eq 18b against y^2; ○, Linear plot of Eq 20. [Points predicted for CH_2 = CHCOR (with R = CMe_2Et and $CMeEt_2$)]

By substituting in Eq 17 for α from Eq 13a and 13b, $A_{C=C}$ can be expressed as a function of $\cos^2 \phi$ where, writing $\cos^2 \phi = y$, f(y) is given by Eq 18b. In Fig 3, f(y) is plotted against y^2. Over the relevant portion, f(y) can be seen (Fig 3) to approximate to the linear function of y expressed in Eq 19. This is equivalent to Eq 20, a relation which was discovered empirically.

$$\text{For } 0{\cdot}49 \leqslant y^2 \leqslant 1: f(y) = -2060y^2 + 2720; r = 0{\cdot}9940 \tag{19}$$

$$A_{C=C} = -44740[(\sigma_R^0)_{tw}]^2 + 2840 = -2145y^2 + 2840 \tag{20}$$

Vinyl ketones: carbonyl intensity. The observed carbonyl intensity will also be the sum of the intensities of the two conformers (Eq 21). We take conformationally homogeneous s-*cis* vinyl t-butyl ketone as a reference point. The $A_{C=O}$ for the unhindered s-*cis* conformers should vary with R as does $A_{C=O}$ for the alkyl methyl ketones (Eq 22), whereas the $A_{C=O}$ for the hindered s-*trans* conformers should vary with R as does $A_{C=O}$ for the phenyl alkyl ketones (Eq 25).

$$A_{C=O}(\text{VyCOR}) = \alpha A_{C=O}(s\text{-}trans\ \text{VyCOR}) + (1 - \alpha)A_{C=O}(s\text{-}cis\ \text{VyCOR}). \tag{21}$$

$$A_{C=O}(s\text{-}cis\ \text{VyCOR}) = \{A^{\ddagger}_{C=O}(s\text{-}cis\ \text{VyCOBu}^t) + [A^{\ddagger}_{C=O}(\text{MeCOR}) - A^{\ddagger}_{C=O}(\text{MeCOBu}^t)]\}^2 \tag{22}$$

$$A_{C=O}(s\text{-}cis\ \text{VyCOR}) = [A^{\ddagger}_{C=O}(\text{MeCOR}) - 1{\cdot}3]^2 \tag{23}$$

$$A_{C=O}(s\text{-}cis\ \text{VyCOBu}^t) = 5330 \tag{24}$$

$$A_{C=O}(s\text{-}trans\ \text{VyCOR}) = \{A^{\ddagger}_{C=O}(s\text{-}trans\ \text{VyCOBu}^t) + [A^{\ddagger}_{C=O}(\text{PhCOR}) - A^{\ddagger}_{C=O}(\text{PhCOBu}^t)]\}^2 \tag{25}$$

Further simplification of Eq 22 and Eq 25 is possible. It is known that vinyl t-butyl ketone exists essentially completely in the s-*cis* conformation, and hence using Eq 24, we can simplify Eq 22 to Eq 23. We treat $A_{C=O}$ for s-*trans* vinyl t-butyl ketone as an adjustable parameter, and by trial and error find Eq 26, which allows simplification of Eq 25 to Eq 27. Substituting Eq 23 and 27 in Eq 21 now gives Eq 28.

$$A_{C=O}(s\text{-}trans\ \text{VyCOBu}^t) = 5625 \tag{26}$$

$$A_{C=O}(s\text{-}trans\ \text{VyCOR}) = [A^{\ddagger}_{C=O}(\text{PhCOR}) - 2{\cdot}6]^2 \tag{27}$$

$$A_{C=O}(\text{VyCOR}) = \alpha[A^{\ddagger}_{C=O}(\text{PhCOR}) - 2{\cdot}6]^2 + (1 - \alpha)[A^{\ddagger}_{C=O}(\text{MeCOR}) - 1{\cdot}3]^2 \tag{28}$$

For the carbonyl stretching bands (unlike the νC=C bands) it is possible to estimate from the spectra rough integrated intensity values for the individual s-*cis* and s-*trans* conformers. Table 6 demonstrates the impressive agreement between observed and calculated values both for the individual conformers and for the total integrated intensity.

An alternative and simpler treatment is to use $A_{C=O}$ for acraldehyde for $A_{C=O}$ s-*trans* and $A_{C=O}$ for t-butyl vinyl ketone for $A_{C=O}$ s-*cis* in Eq 21. This gives Eq 29, which also gives reasonable predicted values of the total νC=O intensity (last column of Table 6) using values of α derived from acetophenone planar (treatment b) but

TABLE 6. VINYL ALKYL KETONES: CARBONYL INTENSITIES

R	α^a	α^b	$A_{C=O}^{s\text{-}cis}$	$(1-\alpha)A^{C=O}_{(s\text{-}cis)}$ calcd.[c]	$(1-\alpha)A^{C=O}_{(s\text{-}cis)}$ obsd.[e]	$A^{C=O}_{s\text{-}trans}$ [g]	$\alpha A^{C=O}_{(s\text{-}trans)}$ calcd.[g]	$\alpha A^{C=O}_{(s\text{-}trans)}$ obsd.[e]	lit.[h]	$A^{C=O}_{(total)}$ obsd.	$A_{C=O}$ calcd.[i]	$A_{C=O}$ calcd.[j]	$A_{C=O}$ calcd.[k]	$A_{C=O}$ calcd.[l]
H	0·97	0·97	5500[d]	160	0	7590	7360	7380	7250	7380	7520	7520	7310	7310
Me	0·86	0·70	5170	1550	1550	6860	4800	4830[f]	4930	6830	5530	6350	7065	6705
Et	0·76	0·53	5130	2410	2900[f]	6270	3320	2650	4800	5750	6000	5730	6840	6320
Pr^i	0·58	0·38	5070	3140	3600[f]	5880	2230	1770	—	5370	5540	5380	6435	5980
Ph	0·30	0·16	—	—	4415[f]	—	—	935	—	5350	—	—	5805	5490
Bu^t	0·16	0·07	5330	4960	5130	5625	390	0	—	5130	5380	5380	5490	5290

[a] From Eq 13a
[b] From Eq 13b
[c] From Eq 23 using $A^{C=O}_{s\text{-}cis}$(Vy COBu^t) = 5330, and α from Eq 13b
[d] Value obtained using Eq 9
[e] Overlapping peaks of carbonyl bands were resolved graphically
[f] Value calculated experimentally only for the main band of the doublet C=O
[g] From Eq 27 using $A^{C=O}_{s\text{-}trans}$ (VyCOBu^t) = 5625, and α from Eq 13b
[h] From Ref 3
[i] From Eq 28 using α from Eq 13a
[j] From Eq 28 using α from Eq 13b
[k] From Eq 29 using α from Eq 13a
[l] From Eq 29 using α from Eq 13b

less satisfactory values (penultimate column of Table 6) using α derived from treatment (a).

$$A_{C=O}(\text{VyCOR}) = \alpha 7380 + (1 - \alpha) 5130 \tag{29}$$

TABLE 7. VINYL ALKYL KETONES. C=O BANDS: FREQUENCY AND ε VALUES

R	$\nu^{\text{cm}^{-1}}_{s\text{-}cis\,(C=O)}$		$\nu^{\text{cm}^{-1}}_{s\text{-}trans\,(C=O)}$		ε_A s-*cis* (C=O)		ε_A s-*trans* (C=O)	
	lit	obsd.	lit	obsd.	lit	obsd.	lit	obsd.
H	—	—	1703[a]	1704	—	—	—	620
Me	1706[a]	1706	1686[a]	1685	—	148	—	388
Et	1707[a]	1706	1690[a]	1688	154[b]	138	227[b]	206
Pr^i	1702[b]	1701	1682[b]	1682	263[b]	247	189[b]	194
Ph	1677[b]	1675	1661[b]	1660	414[b]	400	132[b]	110
Bu^t	1696[b]	1696	—	—	403[b]	414	—	—

[a] From Ref 3

[b] From Ref 9

Infrared frequencies and mechanical coupling. In each series (*i.e.* PhCOR, MeCOR, s-*cis* VyCOR, s-*trans* VyCOR) the νC=O tends to decrease as R increases in size (see Tables 1, 4, 7), but the variations are not large and quantitative correlations were not attempted.

An implicit assumption in the whole of the preceding treatment is the absence of significant mechanical coupling effects on the intensities of the bands. Junge[26] has studied solvent and ^{18}O shifts and concludes that coupling is essentially absent for the s-*trans* conformers, and that, although it does exist to some extent for the s-*cis* conformation, the variations in the band intensities are largely due to other causes, as we have assumed in this paper.

CONCLUSIONS

In this paper we have shown that the observed intensities of the νC=C and νC=O bands in the vinyl alkyl ketones may be explained in terms of conformer populations of s-*cis* and s-*trans* forms of the ketones deduced from energy considerations. We have presented evidence that the s-*cis* conformers are strain-free and have assumed that the steric strain in the s-*trans* conformer is identical to that which occurs in the phenyl alkyl ketones. We further assume that changes of alkyl group from Me to Bu^t do not significantly change the σ°_R of a group COR in a strain free situation. The reported conformational equilibria for acraldehyde and methyl vinyl ketone are interpreted in two extreme ways (a) with the assumption of no difference also between σ°_R for planar CHO and COMe, which implies that the COMe group in acetophenone is twisted 25° out of the plane of the ring, and (b) assuming different σ°_R for CHO and COMe deriving from different conjugative power, the s-*trans* form of methyl vinyl ketone (and also acetophenone) as planar and non-hindered. Our reported calculations have been made for both these two extreme cases; we have shown that the assumption of an intermediate angle of twist for acetophenone and some intrinsic difference in σ°_R for CHO and COMe does not affect the overall general conclusions.

The carbonyl intensity of the s-*cis* form of a vinyl alkyl ketone can be expressed in terms of the corresponding methyl alkyl ketone (Eq 23) and that of the s-*trans* form in terms of the corresponding phenyl alkyl ketone (Eq 27). The total carbonyl intensity for a vinyl alkyl ketone is then given by Eq 28. Good agreement is found with the observed values.

The νC=C intensity for a vinyl alkyl ketone is related to the conformer populations and the $(\sigma^\circ_R)_{tw}$ by Eq 17. As the conformer population can themselves be expressed in terms of $(\sigma^\circ_R)_{tw}$, a complex dependence of the νC=C intensity on $(\sigma^\circ_R)_{tw}$ can be deduced [Eq 18]. It is shown that, over the relevant portion, this complex function is satisfactorily approximated by the linear relation Eq 20.

EXPERIMENTAL

Spectroscopy. IR spectra were recorded using a Perkin Elmer Model 125 spectrometer: each compound was measured in CCl_4 solution and the 1549 cm^{-1} band of the solvent used for balancing the spectrum. For further details see Ref 27. The UV spectra were measured using a Unicam SP 500, (Manual) apparatus, and in EtOH sols.

Compounds. The following commercially available materials were purified by standard methods. Benzaldehyde (b.p. 46°/3 mm); acetophenone (b.p. 74°/5·5 mm); propiophenone (b.p. 87°/5·5 mm); benzophenone (m.p. 48°); phenylacetaldehyde (b.p. 66°/2·5 mm); phenylacetone (b.p. 94°/9·5 mm); acraldehyde (b.p. 53°); methyl vinyl ketone (b.p. 79°); ethyl vinyl ketone (b.p. 99°).

Phenyl alkyl ketones. These ketones were obtained by oxidation of the corresponding secondary alcohols by chromic trioxide[28] and purified by passing them through an alumina column (eluent: CCl_4): isopropyl phenyl ketone: (b.p. 58°/0·3 mm; lit[13] 115°/29 mm); t-butyl phenyl ketone: (b.p. 110°/15 mm; lit[13] 98°/11·5 mm); t-amyl phenyl ketone (b.p. 92°/0·8 mm; lit[28] 118–120°/17 mm) (Found: C, 82·1; H, 9·1. Calcd. for $C_{12}H_{16}O$: C, 81·8; H, 9·2; diethylmethylcarbinyl phenyl ketone (b.p. 102°/0·8 mm) (Found: C, 82·1; H, 10·0. Calcd. for $C_{13}H_{18}O$: C, 82·1; H, 9·5).

Vinyl ketones. Isopropyl vinyl ketone prepared by general method of Ref 29 had b.p. 110–112°/760 mm (lit[30] 50°/90 mm); t-butyl vinyl ketone[31] b.p. 67–68°/105 mm (lit[31] 66–70°/105 mm); phenyl vinyl ketone[32] b.p. 73°/3·5 mm (lit[32] 72–73°/3 mm).

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