SPECTRAL CORRELATIONS FOR β-CHLOROVINYL KETONES

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Abstract—The IR and UV spectroscopic data of a series of alkyl substituted β -chlorovinyl ketones have been determined. Some of the IR and UV spectroscopic criteria, developed for the S-cis or S-trans conformation of ordinary α,β -unsaturated ketones, seem to be applicable for the β chlorovinyl ketones: the S-cis conformer shows a low ratio (r') of the integrated intensities of the carbonyl and double bond stretching vibrations and a relatively low UV ϵ value; whereas high r' and ϵ values are found for the S-trans conformer; non-planarity increases the r' value and decreases the ϵ value.

The prefered conformations as determined by the IR and UV spectral data have led to the presentation of benzene solvation models for a series of β -chlorovinyl ketones. These models made it possible to assign the *cis* or *trans* structure to α,β -dialkyl- β -chlorovinyl ketones on the basis of the NMR aromatic solvent induced shifts of the β -alkyl group: high solvent shifts to a higher field (0.31-0.66 ppm) are found for *cis*- β -chlorovinyl ketones, whereas low solvent shifts (0.040.15) are found for the *trans*- β -chlorovinyl ketones. Assignments based on the chemical shifts alone can lead to erroneous interpretations.

In connection with a study of the mechanism of the AlCl₃-catalyzed addition of acid chlorides to dialkylacetylenes¹, we were interested in an unambiguous method for determining the *cis*-I or *trans*structure II of the β -chlorovinyl ketones formed in this addition.



Since no such method was available, we started a spectroscopic study of these and related β -chlorovinyl ketones.

The NMR spectroscopic data seemed to offer a facile method to distinguish these alkylated β chlorovinyl ketones: because of the deshielding effect of the carbonyl group² on the alkyl group in cis, the protons of this group would resonate at a lower field in the trans isomer. This first interpretation of the NMR spectra¹ could no longer be held for the phenyl β -chlorovinyl ketones, in view of the NMR data we obtained of a series of mono- and dialkylated B-chlorovinyl ketones. A major problem for a correct assignment of the chemical shift values, as well as for a correct interpretation of the aromatic solvent induced shifts, is the conformation of the carbonyl group: S-cis, S-trans or nonplanar. Therefore an IR and UV spectroscopic analysis has been performed.

IR AND UV SPECTROSCOPIC STUDY

Benson and Pohland³ have performed a spectroscopic study of a series of $trans -\beta$ -chlorovinyl ketones (II, R₁ = alkyl, R₂ = R₄ = H), and concluded on the basis of the relatively high UV ϵ -values (ϵ = 14.600-11.200) that these ketones have a planar to nearly planar S-*trans* conformation. However detailed IR studies of Dabrowski and Terpinski⁴ concerning the same β -chlorovinyl ketones indicated the coexistence of a nearly planar S-*trans* form and a planar S-*cis* form.

As models for the S-*cis* and S-*trans* conformers the β -chlorovinyl ketones 1 and 2, with a fixed conformation, and the ketones 3 and 4, with a labile conformation, were synthesized. The ketone 3 is expected to occur predominantly in the S-*cis* conformation, as this is the conformation for mesityl oxide.⁵ The ketone 4 will have an S-*trans* confor-



mation as the isopropenyl methyl ketone has an Strans conformation.⁶

According to Timmons et al.,6 the following criteria can be applied to differentiate between the planar S-cis and S-trans conformation of α,β unsaturated ketones: (1) the ratio of the integrated band intensities of the CO and ethylenic stretching bands, r, lies between 0.6 and 3.5 for S-cis ketones and is greater than 5.2 for S-trans ketones; (2) the wavenumber difference between the C=O and C=C bands $(\Delta \nu)$: greater than 70 cm⁻¹ for S-cis compounds and less than 60 cm⁻¹ for S-trans compounds. Looking at the IR data for compounds 1-5 in Table 1, the rⁱ criterion seems to be applicable for β -chlorovinyl ketones and also for the β chlorovinyl aldehyde 5, although the upper limit of rⁱ for the S-cis conformation and the lower limit of rⁱ for the S-trans conformation have to be lowered somewhat. The $\Delta \nu$ criterion, although in agreement with the IR data of the β -chlorovinyl ketones 1 and

2, with a fixed conformation, is of no utility for the ketones with a labile conformation.

Based on molecular models, the compounds 6 and 7 are further examples of planar or nearly planar respectively S-cis and S-trans conformations. The IR data of the compounds 6 and 7 show that even with a phenyl group present in the molecule, the r^{i} criterion stays applicable, as the aromatic double bond absorptions are small compared to the ethylenic stretching band of the unsaturated ketone.

When another alkyl group is introduced on the double bond, steric interactions cause considerable non-planarity of double bond and CO group. The increased r^i values exclude a planar S-*cis* conformation for the compounds **8**, **9** and **10**, where the substituents R_1 , R_2 and R_4 are responsible for an increasing steric crowding.

On the basis of the rⁱ criterion it is difficult to distinguish between a nearly planar S-*trans* confor-

Table 1 R_1CO $R_2C=C$ R_3

							IR (CCL)			UV	(EtOH)
No.	Rı	R ₂	R ₃	R₄	νc=0	vc=c	Δν	Ĕ	E	r	λ _{max}	ε
1		\bigcirc) =C <t< td=""><td>H C1</td><td>1698</td><td>1580</td><td>108</td><td>6.500</td><td>7-500</td><td>0.9</td><td>245</td><td>7.700</td></t<>	H C1	1 698	1580	108	6.500	7-500	0.9	245	7.700
2					1685	1630	55	12.050	3.380	3.6	241	12.000
3ª	Ме	Н	Cl	Ме	1705 1675(sh)	1610	95	6.250	10.000	0.6	238	7.400
					1710(sh)							
4 [*]	Me	Me	Cl	Н	1685	1610	75	7.450	2.160	3.45	231	15·200
5°	Н	Me	Cl	Me	16 9 0	1628	62	12.970	3.380	3.8	244	12.600
6	Ph	Н	Cl	Et	1672	1605	67	8.400	12.850	0.6	265	16.800
7	Ph	Me	Cl	H	1665	1603	62	7.700	2.850	2.7	246	14.000
8	Me	Me	Cl	Me	1700	1612	88	7.700	6.300	1.2	244	6-060
9	Me	Et	Cl	Et	1698	1610	88	6.850	4.230	1.6	244	5.040
10	Et	Et	Cl	Et	1702	1615	87	6.130	3.620	1.7	243	3.400
11	Ph	ме	CI	ме	1678	1655(sh)	23	8	w	high	249	7.800
					1708	1585	123	S	S			
12 ^a	Me	Н	Cl	Cl	1678	1574	104	m-S	VS	low	241	11.900
13	Ph	·(C]	H₂)₄-	Cl	1675	1655(sh)	20	S	W	high	249	11.700
14	Et	Et	Et	Cl	1706	1645	61	5-080	1.200	4∙2	247	3.600
15	Ph	Me	Me	Cl	1681	1660	21	S	W	high	249	9.500

"Contains according to the NMR spectrum 20% of the cis isomer.

^bContains according to the NMR spectrum 20% of the trans- EtCO-CH=CHCl.

^cThrough cooling on -30° C isolated from a cis-trans mixture as white crystals which liquified again on warming up. Contains according to the NMR spectrum 10% of the cis isomer.

^dIR and UV data of ref. (7) and (8).

mation and a non-planar conformation, as for both conformations high r^i values are found. To distinguish between these conformations the UV ϵ -values can be of some help.

The β -chlorovinyl ketones 2 and 4, and the β chlorovinyl aldehyde 5, all with a planar S-*trans* conformation, show high UV absorbances, whereas the ϵ -values of the β -chlorovinyl ketones 1 and 3, with a planar S-*cis* conformation are much lower. The UV absorbance of the β -chlorovinyl ketones 8, 9 and 10 is still lower and decreases with increasing steric interactions of the substituents R₁, R₂ and R₄. This excludes a nearly planar S-*trans* conformation.

Stuart-Briegleb models show that for $R_2 = R_4$, the S-cis conformation has the least steric hindrance and the CO and double bond can achieve the highest degree of planarity in a conformation close to the S-cis one. Spectroscopic studies showed that for trans- β -chlorovinyl ketones RCO-CH=CHCl, on going from R=Me to R=tBu, the S-cis conformation is favoured.^{4b} Therefore it seems reasonable to attribute a nonplanar S-cis conformation to the β -chlorovinyl ketones 8, 9 and 10, with an increasing degree of non-planarity.

For the compound 11 the rⁱ value could not be determined as the double bond absorption occurred as a shoulder on the CO band, but in any case it is a high value. This together with the low ϵ -value, compared to the planar phenyl β -chlorovinyl ketones, suggests a non-planar conformation. Another class of β -chlorovinyl ketones are the *cis*- β -chlorovinyl ketones. Unfortunately we were not able to prepare *cis*- β -chlorovinyl ketones with an α -H(I, R₂=H), sufficiently pure for IR and UV spectral analyses. These *cis*- β -chlorovinyl ketones are expected to occur in a planar S-*cis* conformation as the steric interaction between R₁ and the β -Cl would make the planar S-*trans* conformation unfavorable.

Good models for these *cis*-compounds are the β , β -dichlorovinyl ketones. A recent IR study of Ellern and Gray⁷ shows that the dichlorovinyl ketone **12** exists, in CCl₄ solution, as a mixture of two conformers: a planar S-*cis* conformer and a non-planar S-*trans* conformer. Taking into account a hyperchromic effect of the second β -chlorine,⁸ the UV ϵ -value of this compound is too low for an S-*trans* conformation (*cf* compound 4). For the phenyl β , β -dichlorovinyl ketone, dipole moment data point to an S-*cis* conformation, whereas substitution of the α -H by a Me group results in non-planar conformations.⁸

As a model compound for the dialkylated $cis-\beta$ chlorovinyl ketones we synthesized the compound 13. The rⁱ value could not be determined as the C=C absorption was to small and occurred as a shoulder on the carbonyl absorption band. This high rⁱ value suggests a non-planar or an S-trans conformation. The $cis-\beta$ -chlorovinyl ketone 14 should be classified definitely as non-planar, regarding its low UV ϵ value and its high rⁱ value.

As a conclusion of this IR and UV spectroscopic study can be said that in CCL solution:

(1) trans- β -Chlorovinyl ketones with an α -H(R₂ = H) have a planar S-cis conformation; the *cis*-isomers have an average conformation between a planar S-*cis* and a non-planar S-*trans* conformation.

(2) trans- β -Chlorovinyl ketones with a β -H(R₄ = H) and an α -alkyl group have a planar to nearly planar S-trans conformation.

(3) cis- and trans- β -Chlorovinyl ketones with R₂ and R₃ (or R₄) different from hydrogen, have non-planar conformations.

NMR SPECTROSCOPIC STUDY

No special difficulties are encountered in the assignment of cis- and trans-structures to β chlorovinyl ketones with an α -hydrogen (I, R₂=H; II, R₂=H). As we know from our IR and UV investigations, these β -chlorovinyl ketones have an S-cis conformation (most certain for the *trans* isomers). For this conformation the model of Jackman, describing the magnetic anisotropy of the carbonyl group,² predicts an NMR deshielding influence of the carbonyl function on the β -hydrogen and the hydrogens of the cis- β -alkyl group (R₄ in II). This deshielding effect results in a low field absorption of \mathbf{R}_4 in the *trans*- β -chlorovinyl ketones. This is confirmed by the results in the first part of Table 2, which also contains the NMR data of some model compounds (1, 16 and 17) with a fixed S-cis conformation. A confirmation of the mainly S-cis conformation of these compounds is found when we compare, in Table 2, the phenyl ketones $(R_1 = Ph)$ with and methyl ketones $(R_1 = Me)$: 18 and 19 with 22 and 3, and 21 with 23. For the phenyl ketones the α -H(R₂) absorbs at a much lower field than for the methyl ketones. This can be explained by a deshielding influence of the phenyl group in a planar S-cis conformation.

Another class of β -chlorovinyl ketones are those with a β -hydrogen (compounds 7, 24; and 4). As already mentioned in the IR and UV study, for these compounds a planar S-trans conformation is the most favorable. Also the β -chlorovinyl aldehvde 5 is expected to occur predominantly in the S-trans conformation, as, according to molecular models, the most important steric interactions, between the CO oxygen and the α - and β -Me groups are at a minimum in the S-trans conformation. The assignment of cis- and trans structures poses no difficulties as even in α,β unsaturated ketones with an S-trans conformation, a deshielding effect on the group in cis of the CO can be expected.9 Comparing the phenyl ketone 7 with the methyl ketone 4, the β -hydrogen (R₄) of the methyl ketone



						δ (pp				
No.	R,	R ₂	R ₃	R₄	Isomer	R.	R ₂	R ₃	— R₄	Solvent
1		\leq	=c< ^H	l	trans	2.22-	2.82		7.15	CDCl ₃
16"	Ć			_н `СI	trans	-	3.7	-	7.35	-
17ª	Ć	X	,0 ≽=c<	Cl H	cis		3.7	6.45		_
18 19 20 6 21 ^b 22 3 23 ^b 7 24 ^c 4 5 ^d 25 ^d	Ph Ph Ph Me Me Ph Ph H H	H H H H H H Me Me Me Me	Me Cl Cl Cl Cl Cl Cl Cl Cl Cl H Cl Cl Me	Cl Me Cl Cl Cl Cl H Cl H Cl H Cl	cis trans cis trans cis trans cis trans cis trans cis		6.80 7.15 6.82 7.08 7.16 6.27 6.47 6.47 6.61 2.12 1.96 1.94 1.88 1.81	$ \begin{array}{c} 2 \cdot 27 \\ - 2 \cdot 56 \\ - \\ 2 \cdot 26 \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ -$	2.60 2.97 2.52 6.89 7.29 2.64 -	CDCl ₃ CDCl ₃ CDCl ₃ CCL ₄ CDCl ₃ CDCl ₃ CCL ₄ CDCl ₃ CCL ₄ CDCl ₃ CCL ₄ CDCl ₃

^e Data of Ref (2) p. 223.

^bData of Ref (8).

^cData of Ref (20).

^dData of Ref (15).

absorbs at a lower field than that of the phenyl ketone. This seems reasonable to us, as in an *S*-trans conformation the steric hindrance between the phenyl group and the β -hydrogen ^{3.4a} forces the phenyl group out of the plane of the double bond, resulting in a shielding rather than a deshielding influence of the phenyl group on the β -hydrogen.

When both positions, α and β , are alkyl substituted, steric interactions, between R_1 and R_2 and R_4 in the *trans* isomer, and between R_1 and R_2 and Clin the *cis* isomer, will be considerable. Non-planar conformations will make it difficult to predict the deshielding or shielding influence of the carbonyl function on the α - and β -alkylgroups¹⁰. As for these ketones the mesomeric interaction between the double bond and the CO is small, the β -alkyl group absorbs at a higher field. This makes it difficult to distinguish the absorptions of α - and β -alkyl groups. The δ values in Table 3 have been assigned in such a way that a coherent system was obtained. In Table 3 we find also the NMR data of

some model compounds. The methyl β , β dichlorovinyl ketone 30 and the phenyl β , β dichlorovinvl ketone 31 are good model compounds for the $cis-\beta$ -chlorovinyl ketones 26 and 15. The methyl ketone 32 and the phenyl ketone 33 are model compounds for the trans-\$-chlorovinyl ketones 8 and 11. The conformation of the Me and phenyl β , β -dichlorovinyl ketones has been investigated by Sanchez⁸, who concluded that these compounds have non-planar conformations. The difference in chemical shift of R₂ for these two ketones suggests nevertheless a different orientation of the CO function. The same difference is also found for the β -chlorovinyl ketones 26 and 15, and 27 and 28, suggesting the same difference in conformation. On the basis of NMR benzene solvent shifts, Timmons¹¹ classifies the methyl ketone 32 as a nonplanar S-cis conformer. The δ values for the phenyl ketone 33 have been secured by measuring the different homoallylic coupling constants on a 100 MHz spectrum: the homoallylic coupling con-

Table 3. NMR data of



						δ				
No.	R	\mathbf{R}_2	R ₃	R₄	Isomer	R,	R ₂	R ₃		Solvent
26 8 15 11	Me Me Ph Ph	Me Me Me Me	Me Cl Me Cl	Cl Me Cl Me	cis trans cis trans	2·41 2·33	1.88 2.04 1.98 2.05	2·19 2·25	2.33 $\overline{2.05}$	CDCl ₃ CDCl ₃ CDCl ₃ CDCl ₃
2		O= Me			trans	_	1.88	_		CDCl ₃
27 9 28 29 30 ^a 31 ^a 32 ^b 33	Me Ph Ph Me Ph Me Ph	Et Et Et Me Me Me	Et Cl Cl Cl Cl Me Me	Cl Et Cl Et Cl Cl Me Me	cis trans cis trans — — —	2.32 2.22 2.35 - 2.11	2·27 2·45 2·40 2·52 1·98 2·10 1·82 1·87	2·44 	2·45 	CDCl ₃ CDCl ₃ CDCl ₃ CDCl ₃ CCl ₄ CCl ₄ CCl ₄ CCl ₄ CDCl ₃

"NMR data of Ref 8.

^b Data of Ref 10. There exist a different interpretation of the σ -values by Timmons, Ref 11, who assigns the δ -value 1.76 to the α -Me group R₂. This results in no deshielding influence of the acetyl group instead of the low deshielding influence proposed in Ref 9.

stant for Me groups in *trans* is always by 0.3 c/s larger than for Me groups in cis¹². These homoallylic coupling constants constitute in fact a method for assigning cis- or *trans*-structure for β chlorovinyl ketones with Me groups on the α and β positions: the compounds 25, 26 and 15 have homoallylic coupling constants of respectively 1.0 c/s, 1.15 c/s and 1.1 c/s; the corresponding trans isomers 5, 8 and 11 have coupling constants of respectively 1.5 c/s, 1.6 c/s and 1.5 c/s. The Me absorptions of the phenyl ketone 33 at 1.87 ppm (R₂) and 1.61 ppm (R₄) have a homoallylic coupling constant of 1.5 c/s, which means that they are located *trans* to another.

Comparing now the δ -values, which have been assigned to the R₃ and R₄ alkyl groups in compounds **32** and **33**, it is obvious that an acetyl has a small deshielding effect of 0.06 ppm on the Me in *cis*, whereas a benzoyl has a shielding effect of 0.23 ppm on the Me in *cis*. The NMR data of the other β -chlorovinyl ketones in Table 3 have been interpreted with these deshielding and shielding effects of acetyl and benzoyl groups. It has to be noted that this shielding instead of a deshielding effect of a benzoyl group, led to our wrong first interpretation of the NMR data of *cis*- and *trans*- α,β -diëthyl- β chlorovinyl phenyl ketones¹.

Another possibility to determine the relative pos-Tetra Vol. 29 No. 24-N

itions of hydrogens and alkyl groups in a molecule containing a CO function is the through aromatic solvents induced solvent shift (ASIS) of the NMR signals of these hydrogens and alkyl groups¹³. This method has already been applied in the conformational analysis of α,β -unsaturated ketones¹¹, in the determination of the cis or trans structure of α,β unsaturated ketones¹⁴ and of β -chlorovinyl al-dehydes¹⁵. Chau *et al*¹⁶ found that in the solvation of polar molecules by benzene, the benzene molecules arrange themselves parallel to the resultant of the different dipole moments and in such a way that the interaction of the π -electron cloud with other negative centers in the molecule is at a minimum. Steric interactions by bulky substituents can prevent the benzene molecules from approaching as close to the CO function as they would in an unsubstituted molecule. They will approach at a steeper angle to the plane of the solute molecule¹¹. In Table 4 we have listed the NMR benzene induced shifts of a series of β -chlorovinyl ketones and related compounds with a planar or nearly planar S-cis of S-trans conformation. For the β chlorovinyl ketones with an S-trans conformation (2, 4 and 7) the solvation models proposed for cisand *trans*- β -chlorovinyl aldehydes¹⁵, seem to be applicable. These solvation models result in a shielding effect for \mathbf{R}_4 and little or no effect for \mathbf{R}_2 in

Table 4. NMR solvent shifts of



						Δ in	ppm, or	of -H₁,· -CH₃	-CH ₂ -		
No.	R,	R ₂	R,	R₄	Isomer	R,	R ₂	R ₃	_ R₄	shift	model
25°	н	Me	Me	Cl	cis		0.20	0.40		CCl₄-C ₆ D ₆	1b
5°	Н	Me	Cl	Me	trans		0.05	—	0.44	CCL-C ₆ D ₆	1a
2		0= Me	=	l	trans		0.03			$\begin{array}{c} CDCl_3 \rightarrow \\ C_6D_6 \end{array}$	la
4	Me	Me	Cl	н	trans		0.15	_	0.65	CDCl ₃ -C ₆ D ₆	1a
7	Ph	Me	Cl	н	trans		0.12	—	0.37	CDCl ₃ -C ₆ D ₆	1a
18	Ph	H	Me	Cl	cis		0.40	0.47	_	CDCl ₃ -C ₆ D ₆	1c
20	Ph	н	Et	Cl	cis		0.44	0.46	_	CDCl ₃ -C ₆ D ₆	1c
22	Me	Н	Me	Cl	cis		0.39	0.46		CDCl ₃ -C ₆ D ₆	1c
19	Ph	Н	Cl	Me	trans		0.15	_	0.15	CDCl ₃ -C ₆ D ₆	1d
6	Ph	н	Cl	Et	trans		0.17	—	0.06	CDCl ₃ -C ₆ D ₆	1d
3	Me	Н	Cl	Me	trans		0.31	_	0.15	CDCl ₃ -C ₆ D ₆	1 d
1	(\bigcirc	- -<'	H C1	trans				0.04	CDCl ₃ -C ₆ D ₆	1đ

^a From Ref 15. The solvent shifts are obtained by only a partial replacement of CCl₄ by C₆D₆. ^b $\Delta = \delta_{CoCl_3} - \delta_{C_6D_6}$.

the case of *trans*- β -chlorovinyl ketones (Fig 1a), and a shielding effect for R₂ and R₃ in the case of the *cis*- β -chlorovinyl ketones (Fig 1b).

With $R_1 = Ph$, the repulsion between the π -electron cloud of the phenyl group and the solvating benzene molecule, ¹⁶ will prevent a close approach, and the solvent shifts of R_4 will be smaller (compound 7 in Table 4).

For cis- and trans- β -chlorovinyl ketones (18 to 1) with a planar S-cis conformation, we propose the solvation models as depicted in Fig 1c and 1d. In 1c the dipoles are parallel and the solvating benzene molecules are far from the negative centers in the molecule, making a close approach and consequently high solvent shifts possible.

Contrary, in 1d the dipoles are not parallel and the solvating benzene molecules are prevented

from a close approach by the chlorine and oxygen atoms, the negative ends of the dipoles. As a result only small solvent shifts can be expected. The solvation models for cis- and trans-B-chlorovinyl ketones with non-planar conformations will resemble those depicted in Fig 1, but as a result of increased steric hindrance one would expect decreased solvent shifts. This is clearly demonstrated by comparing the solvent shifts of the β chlorovinyl ketones 26, 34 and 35 in Table 5: the increasing steric hindrance between R1 and R2 will decrease the planarity of the enone system and consequently decrease the observed solvent shifts. The high solvent shifts of R_2 and R_3 , found for the methyl β -chlorovinyl ketone 26, are in agreement with solvation model 1c, pointing to an S-cis conformation. The other $cis-\beta$ -chlorovinyl ketones



Fig 1.

Table 5. NMR solvent shifts of



						Δ -C	in ppm c CH2-or-CH	of I3		
No	R,	R ₂	R ₃	R₄	Isomer	R ₂	R ₃	R₄	shift	model
26	Me	Ме	Ме	Cl	cis	0.66	0.66	_	CDCl ₃ -C ₆ D ₆	1c
34	CH ₂ Cl	Me	Me	Cl	cis	0.34	0.41	_	CDCl ₃ -C ₆ D ₆	1c
35	CHCl ₂	Me	Me	Cl		0.23	0.31	—	CDCl ₃ -C ₆ D ₆	1c
27	Me	Et	Et	Cl	cis	0.41	0.47		CDCl ₃ -C ₆ D ₆	1c
15	Ph	Me	Me	Cl	cis	0.39	0.50	—	CDCl ₃ -C ₆ D ₆	1a-1c
28	Ph	Et	Et	Cl	cis	0·27	0.38	—	CDCl ₃ -C ₆ D ₆	1a-1c
13	Ph	-(C)	I ₂)₄-	Cl	cis	=C-CI	I₂-CH₂ 0·46		CDCl ₃ -C ₆ D ₆	la-lc
8	Me	Me	Cl	Me	trans	0.28	_	0.15	CDCl ₁ -C ₆ D ₆	1d
9	Ме	Et	Cl	Et	trans	0.15		0.07	CDCl ₁ -C ₆ H ₆	1d
32°	Ме	Me	Me	Ме	_	0.40	0.19	0.02	CClC6H6	
11	Ph	Me	Cl	Ме	trans	0.21		0.11	CDCl ₁ -C ₆ D ₆	1b-1d
29	Ph	Et	Cl	Et	trans	0.10		0.04	CDCl ₃ -C ₆ D ₆	1b-1d
33	Ph	Me	Me	Me	_	0.13	0-28	0.11	CDCl ₃ -C ₆ D ₆	

"The solvent shifts denoted have been calculated from the NMR data of ref 10 in CCL and the NMR data of ref 11 in C_6H_6 .

show solvent shifts which are somewhat smaller, expecially the solvent shift of R_2 . This decrease in solvent shift can be explained by steric interference to solvation or perhaps by a solvation model which is more close to 1b than to 1c, resulting also in a marked decrease in solvent shift for R_2 (cfr compound 25 in Table 4).

The solvent shifts observed for the methyl β chlorovinyl ketone 8 and the phenyl β -chlorovinyl ketone 11 can be compared with those of the respective model compounds 32 and 33. The solvent shifts observed for the phenyl ketone 33 are apparently different from those of the methyl ketone 32, suggesting a different conformation. In his conformational study of α , β -unsaturated ketones, Timmons¹¹ developed the following criteria for assigning conformations on the basis of NMR solvent shifts induced by benzene: S-cis conformations give large solvent shifts for R₂ and R₃ and small or negative shifts for R₄, while S-trans conformations give large solvent shifts for R₃, relatively large solvent shifts for R₄ and a small one for R₂. On this basis he attributed a non-planar S-cis conformation to the methyl ketone 32. For the phenyl ketone 33 a non-planar S-trans conformation seems most reasonable. This different conformation explains the shielding effect of the benzoyl group on cisalkyl groups in this model compound 33 and in the other trans β -chlorovinyl ketones as already mentioned in the discussion of Table 3. In any case it seems safe to us to conclude that cis- α , β dialkyl β -chlorovinyl ketones show markedly larger solvent induced NMR shifts for R₃ (0.31-0.66 ppm), than the trans isomers (0.04-0.15 ppm) for R₄.

As a final proof of the *cis* and *trans* structure of these α , β -dialkyl- β -chlorovinyl ketones, the following unambiguous synthesis for two *cis*- *trans* pairs of these ketones was accomplished. Starting from a *cis*- *trans* mixture of 3-chloro-2-methyl-2-butenal (25/5), with a known *cis*- *trans* proportion¹⁵, the β -chlorovinyl ketones 8/26 and 11/15 were obtained with the same *cis*-*trans* proportion, according the following scheme:



Finally, a simple method to distinguish cis- and $trans-\beta$ -chlorovinyl ketones, provided both isomers are available and do not isomerize, is to determine their retention times on a carbowax GLC column or their R_f values on a silicagel thin layer with CCL₄-C₆H₆(1/1): the product with the smallest retention time and the highest R_f value is the trans isomer.

EXPERIMENTAL

The IR spectra have been recorded with a Perkin Elmer 257 grating spectrophotometer. The apparent molar absorptivities (ϵ) were calculated from $\epsilon = \frac{\log_{10} (T^{\circ}/T)}{cl}$, $c = concentration in mol 1^{-1}$, 1 = the cell path length in cm. The apparent integrated intensity was calculated from $E = K \Delta \nu_{1}$. ϵ , where $\Delta \nu_{1}$ is the apparent half-band width in cm⁻¹ and K was taken equal to 1.27 as in ref 6.

The UV spectra have been taken on a Perkin Elmer 402 UV spectrophotometer. The NMR spectra have been recorded on a Varian A-60 (60MHz) and on a Varian XL-100 (100MHz) spectrometer.

 β -chlorovinyl ketone 1. Thionyl chloride (7.6 ml; 0.1 mole) in 50 ml dry benzene was added slowly to α -formyl-cyclohexanone¹⁷ (12.6 g; 0.1 mole) in 50 ml dry benzene. The temp was kept below 10° by cooling with an ice bath. After standing overnight at room temp, the benzene soln was washed with ice-water until the water was neutral. The benzene was evaporated under vacuum and the residue was distilled on a "Büchi-Kugelrohr" distillation apparatus (oven temp 100°, 0.1 mm Hg). The slightly coloured liquid was immediately used for the spectroscopic measurements, as it decomposed within one day, leaving a black polymer. β -chlorovinyl ketone 2. This ketone has been obtained by the method of Frank and Hall¹⁸ from 2-methyl-1, 3cyclohexanedione, with PCl₃. The product was purified by distillation on a "Kugel-rohr" (oventemperature 135°, 30 mm Hg).

B-chlorovinyl ketones 3, 6, 8-11, 14, 15, 18-20, 22, 27-29, 34, 35 All these β -chlorovinyl ketones have been obtained through the AlCl₃ catalysed addition of acid chlorides to acetylenes. Acid chloride (0.01 mole) and AlCl₃ (0.01 mole) in 25 ml dry dichloromethane were stirred at room temp until all the AlCl, had dissolved. This soln was cooled to -30° and 0.01 mole acetylene derivative dissolved in 25 ml dry dichloromethane was added slowly (0.5 hr). When all the acetylene was added the mixture was allowed to warm up to room temp and the AlCl₃complex was decomposed with a mixture of ice HCl 10%. The organic layer was washed successively with water, NaHCO₃ aq and water. After drying on anhyd MgSO₄ the dichloromethane soln was concentrated under vacuum and the residue was distilled under vacuum on a "Büchi Kugelrohr" distillation apparatus.

These liquids were subjected to a preparative GLC separation with a 6 ft carbowax 20M/TFA 20% column on a Varian Autoprep. 713 instrument (a) or to a preparative TLC separation on silica gel with $CCl_*-C_*H_6(1/1)$ as eluens (b) or to a combination of both. The purification methods, which were used for the different β -chlorovinyl ketones, can be found in the table below.

 β -chlorovinyl ketone 4. This β -chlorovinyl ketone was obtained in the same manner as compound 1, from the formylation product of 2-butanone¹⁹. After distillation on a "Büchi-Kugelrohr", (90°, 30 mm Hg), the liquid was purified by a GLC separation on a 6 ft OV-17 5% column at 50°. This purification step could not remove the isomeric ethyl β -chlorovinyl ketone (20%), resulting from

Compound	Distillation: Oven temp, °C vacuum, mm Hg	Chromatographic purification					
3 + 22	80°, 30 mm	cis-trans mixture, $80\% 3 + 20\%$					
6 + 20	120°, 1 mm	(b) afforded two fractions: pure 6 and a mixture of 20 and a β , γ - unsaturated ketone.					
8	90°, 15 mm	no purification required					
9 + 27	90°, 5 mm	(a) afforded two fractions: pure 9, and a second fraction consisting of 27 with some β, γ -unsaturated ketone as impurity					
10 + 14	-	(a) afforded three fractions: pure 10, pure 14 and pure 2,3 dië- thylcyclopentenone					
11 + 15	100°, 0∙8 mm	(b): pure 11 and a mixture of 15 and the yellow 2,3 dimethyl inde- none, which was separated by me- thod (a)					
18 + 19	90°, 0·1 mm	(b): two fractions: 18 with some 19 and 19 with some 18.					
28 + 29	—	(b): pure 28 and a mixture of 29 and the yellow 2,3 diethylindenone which was separated by method (a).					
34	140°, 10 mm	cis-trans mixture, no further					
35	—	(b): pure 35 as main fraction.					

the concurrent formylation of 2-butanone at the 1-position.

 β -chlorovinyl aldehydes 5 and 25. These compounds were synthesized according to a described procedure¹⁵, which afforded a mixture of 29% cis and 71% trans isomer. The trans isomer could be obtained in a 90% purity by freezing out the trans isomer at -30° and decanting the liquid cis isomer.

 β -chlorovinyl ketone 7. This β -chlorovinyl ketone was synthesized as described by Nesmeyanov *et al*²⁰, bp 150°, 40 mm Hg. In contrast to these authors we were not able to isolate the *cis* isomer.

β-chlorovinyl ketone 13. Ph Mg Br (0.28 mole) in 300 ml dry ether was added slowly to a cooled soln of 2chloro-cyclohex-1-enecarbaldehyde (40 g; 0.28 mole) in 300 ml dry ether. The temp was kept between -30° and - 20°. After all the organo-magnesium soln was added, the mixture was warmed up and stirred for 1 hr at room temp. The organomagnesium soln was decomposed with a satd. NH₄Cl aq, as described²¹. The resulting product was distilled under vacuum (155°, 1 mm): $52 \cdot 5 \text{ g}$ (yield 84%). This benzylic alcohol was dissolved in 150 ml acetone and 60 ml Jones reagent²² was added slowly, while the mixture was cooled in an ice bath. After all the oxidant had been added the mixture was kept for 1 hr at room temp. The organic layer was decanted in one liter water and extracted 4 times with 250 ml dichloromethane. The extracts were washed with Na HCO₃ aq, water and then dried on anhyd MgSO4 and concentrated under vacuum. The residue was distilled under vacuum (155°, 1 mm): 40 g (yield = 76%).

 β -chlorovinyl ketones 8 and 26 from the β -chlorovinyl aldehydes 5 and 25. The same procedure with 3-chloro-2-methylbut-2-enal¹⁵ (71% trans 5, 29% cis 25) and with MeMgI in THF afforded a mixture of 8 and 26, respectively 76% and 24%, according to a GLC analysis on a 6 ft Carbowax 20 M TFA 20% column at 100°. Compound 26 and 8 were isolated by a preparative GLC separation of the mixture on the same column at the same conditions.

 β -chlorovinyl ketones 11 and 15 from the β -chlorovinyl aldehydes 5 and 26. The same procedure with PhMgBr in ether, afforded a mixture of 11 and 15, respectively 75% and 25% according to a GLC analysis on a 6 ft Carbowax 20 M/TFA 10% column at 150°. The compounds 11 and 15 were isolated by a preparative GLC separation, and were proven to be identical with the β -chlorovinyl ketones isolated in the AlCl₃ catalysed addition of benzoyl chloride to 2-butyne.

Compound 33. This was prepared by addition of benzoyl chloride to 2-methyl-2-butene and dehydrochlorination of the β -chloroketone according the procedure of Colonge and Chambion²³. The product was distilled under vacuum (140°, 18 mm). A chromatographic separation on a silicagel thinlayer with CCl₄-C₆H₆(1/1) eliminated the 2,3,3,'-trimethylindanone, formed in the reaction but left 33 contaminated with the dehydrochlorination product of the anti-Markownikoff addition product. This was effectively removed by a GLC separation on a 6 ft OV-17 5% column at 130°.

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