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SPECTRAL CORRELATIONS FOR β-CHLOROVINYL KETONES

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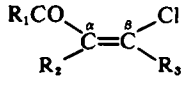
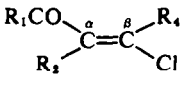
Abstract—The IR and UV spectroscopic data of a series of alkyl substituted β-chlorovinyl ketones have been determined. Some of the IR and UV spectroscopic criteria, developed for the S-*cis* or S-*trans* conformation of ordinary α,β-unsaturated ketones, seem to be applicable for the β-chlorovinyl ketones: 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 $AlCl_3$-catalyzed addition of acid chlorides to dialkylacetylenes[1], 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.



I



II

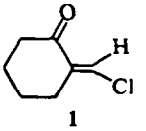
Since no such method was available, we started a spectroscopic study of these and related β-chlorovinyl ketones.

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 group[2] 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 spectra[1] 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 β-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 non-planar. Therefore an IR and UV spectroscopic analysis has been performed.

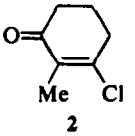
IR AND UV SPECTROSCOPIC STUDY

Benson and Pohland[3] have performed a spectroscopic study of a series of *trans*-β-chlorovinyl ketones (II, R_1 = alkyl, $R_2 = R_4 = H$), 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 Terpinski[4] 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-



1



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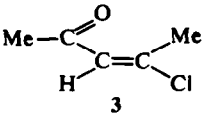

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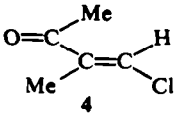


4

mation as the isopropenyl methyl ketone has an S-*trans* conformation.[5]

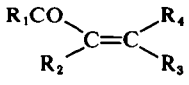
According to Timmons *et al.*,[6] the following criteria can be applied to differentiate between the planar S-*cis* and S-*trans* conformation of α,β-unsaturated ketones: (1) the ratio of the integrated band intensities of the CO and ethylenic stretching bands, r, lies between 0·6 and 3·5 for S-*cis* 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 r^i criterion seems to be applicable for β-chlorovinyl ketones and also for the β-chlorovinyl aldehyde **5**, although the upper limit of r^i for the S-*cis* conformation and the lower limit of r^i 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.

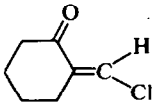
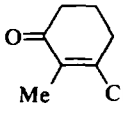
Based on molecular models, the compounds **6** and **7** are further examples of planar or nearly planar respectively S-*cis* and S-*trans* conformations. The IR data of the compounds **6** and **7** show that even with a phenyl group present in the molecule, the r^i criterion stays applicable, as the 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 r^i criterion it is difficult to distinguish between a nearly planar S-*trans* confor-

Table 1



No.	R_1	R_2	R_3	R_4	IR (CCl_4) νC=O	νC=C	Δν	$E_{c=o}$	$E_{c=c}$	r_i	UV (EtOH) λ_{max}	ε
1					1698	1580	108	6·500	7·500	0·9	245	7·700
2					1685	1630	55	12·050	3·380	3·6	241	12·000
3[a]	Me	H	Cl	Me	1705 1675(sh)	1610	95	6·250	10·000	0·6	238	7·400
					1710(sh)							
4[b]	Me	Me	Cl	H	1685	1610	75	7·450	2·160	3·45	231	15·200
5[c]	H	Me	Cl	Me	1690	1628	62	12·970	3·380	3·8	244	12·600
6	Ph	H	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	Me	Cl	Me	1678	1655(sh)	23	S	W	high	249	7·800
					1708	1585	123	S	S			
12[d]	Me	H	Cl	Cl	1678	1574	104	m-S	VS	low	241	11·900
13	Ph	$-(CH_2)_4-$		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

[a] Contains according to the NMR spectrum 20% of the cis isomer.
[b] Contains according to the NMR spectrum 20% of the trans- EtCO—CH=CHCl.
[c] Through 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.
[d] IR and UV data of ref. (7) and (8).

mation and a non-planar conformation, as for both conformations high r' 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 R_1, R_2 and R_4. 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 non-planar S-*cis* conformation to the β-chlorovinyl ketones **8**, **9** and **10**, with an increasing degree of non-planarity.

For the compound **11** the r' 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, R_2=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 R_1 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 Gray[7] shows that the dichlorovinyl ketone **12** exists, in CCl_4 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*-β-chlorovinyl ketones we synthesized the compound **13**. The r' 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 r' value suggests a non-planar or an S-*trans* conformation. The *cis*-β-chlorovinyl ketone **14** should be classified definitely as non-planar, regarding its low UV ε value and its high r' value.

As a conclusion of this IR and UV spectroscopic study can be said that in CCl_4 solution:

(1) *trans*-β-Chlorovinyl ketones with an α-H(R_2 = 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(R_4 = H) and an α-alkyl group have a planar to nearly planar S-*trans* conformation.

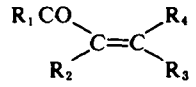
(3) *cis*- and *trans*-β-Chlorovinyl ketones with R_2 and R_3 (or R_4) different from hydrogen, have non-planar conformations.

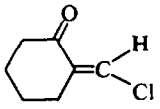
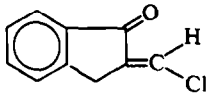
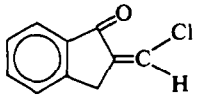
NMR SPECTROSCOPIC STUDY

No special difficulties are encountered in the assignment of *cis*- and *trans*-structures to β-chlorovinyl ketones with an α-hydrogen (I, R_2=H; II, R_2=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,[7] predicts an NMR deshielding influence of the carbonyl function on the β-hydrogen and the hydrogens of the cis-β-alkyl group (R_4 in II). This deshielding effect results in a low field absorption of 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(R_2) 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 aldehyde **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 (R_4) of the methyl ketone

Table 2. NMR data of



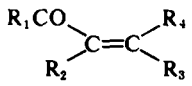
No.	R_1	R_2	R_3	R_4	Isomer	δ (ppm) of -H_1, -CH_2- or -CH_3 R_1	R_2	R_3	R_4	Solvent
1					*trans*	2·22–2·82		—	7·15	$CDCl_3$
16[a]					*trans*	—	3·7	—	7·35	—
17[a]					*cis*	—	3·7	6·45	—	—
18	Ph	H	Me	Cl	*cis*	—	6·80	2·27	—	$CDCl_3$
19	Ph	H	Cl	Me	*trans*	—	7·15	—	2·60	$CDCl_3$
20	Ph	H	Et	Cl	*cis*	—	6·82	2·56	—	$CDCl_3$
6	Ph	H	Cl	Et	*trans*	—	7·08	—	2·97	$CDCl_3$
21[b]	Ph	H	Cl	Cl	—	—	7·16	—	—	CCl_4
22	Me	H	Me	Cl	*cis*	2·33	6·27	2·26	—	$CDCl_3$
3	Me	H	Cl	Me	*trans*	2·20	6·47	—	2·52	$CDCl_3$
23[b]	Me	H	Cl	Cl	—	2·29	6·61	—	—	CCl_4
7	Ph	Me	Cl	H	*trans*	—	2·12	—	6·89	$CDCl_3$
24[c]	Ph	Me	H	Cl	*cis*	—	1·96	6·20	—	CCl_4
4	Me	Me	Cl	H	*trans*	2·33	1·94	—	7·29	$CDCl_3$
5[d]	H	Me	Cl	Me	*trans*	10·07	1·88	—	2·64	CCl_4
25[d]	H	Me	Me	Cl	*cis*	10·22	1·81	2·41	—	CCl_4

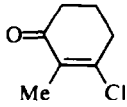
[a] Data of Ref (2) p. 223.
[b] Data of Ref (8).
[c] Data of Ref (20).
[d] Data of Ref (15).

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 Cl in 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-alkylgroups[10]. 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-dichlorovinyl ketone **31** are good model compounds for the *cis*-β-chlorovinyl ketones **26** and **15**. The methyl ketone **32** and the phenyl ketone **33** are model compounds for the *trans*-β-chlorovinyl ketones **8** and **11**. The conformation of the Me and phenyl β,β-dichlorovinyl ketones has been investigated by Sanchez[8], who concluded that these compounds have non-planar conformations. The difference in chemical shift of R_2 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, Timmons[11] classifies the methyl ketone **32** as a non-planar 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



No.	R_1	R_2	R_3	R_4	Isomer	δ in ppm, CH_3-or-CH_2- R_1	R_2	R_3	R_4	Solvent
26	Me	Me	Me	Cl	*cis*	2·41	1·88	2·19	—	$CDCl_3$
8	Me	Me	Cl	Me	*trans*	2·33	2·04	—	2·33	$CDCl_3$
15	Ph	Me	Me	Cl	*cis*	—	1·98	2·25	—	$CDCl_3$
11	Ph	Me	Cl	Me	*trans*	—	2·05	—	2·05	$CDCl_3$
2					*trans*	—	1·88	—	—	$CDCl_3$
27	Me	Et	Et	Cl	*cis*	2·32	2·27	2·44	—	$CDCl_3$
9	Me	Et	Cl	Et	*trans*	2·22	2·45	—	2·45	$CDCl_3$
28	Ph	Et	Et	Cl	*cis*		2·40	2·55	—	$CDCl_3$
29	Ph	Et	Cl	Et	*trans*		2·52	—	2·20	$CDCl_3$
30[a]	Me	Me	Cl	Cl	—	2·35	1·98	—	—	CCl_4
31[a]	Ph	Me	Cl	Cl	—	—	2·10	—	—	CCl_4
32[b]	Me	Me	Me	Me	—	2·11	1·82	1·76	1·82	CCl_4
33	Ph	Me	Me	Me	—		1·87	1·84	1·61	$CDCl_3$

[a] NMR data of Ref 8.

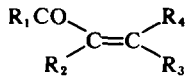
[b] Data of Ref 10. There exist a different interpretation of the σ-values by Timmons, Ref 11, who assigns the δ-value 1·76 to the α-Me group R_2. This results in no deshielding influence of the acetyl group instead of the low deshielding influence proposed in Ref 9.

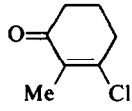
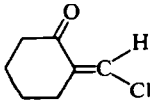
stant for Me groups in *trans* is always by 0·3 c/s larger than for Me groups in *cis*[12]. These homoallylic coupling constants constitute in fact a method for assigning *cis*- or *trans*-structure for β-chlorovinyl ketones with Me groups on the α and β positions: the compounds **25**, **26** and **15** 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 (R_2) and 1·61 ppm (R_4) have a homoallylic ccoupling 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 R_3 and R_4 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 ketones[1].

Another possibility to determine the relative positions 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 groups[13]. This method has already been applied in the conformational analysis of α,β-unsaturated ketones[11], in the determination of the *cis* or *trans* structure of α,β-unsaturated ketones[14] and of β-chlorovinyl aldehydes[15]. 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 molecule[11]. 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 *cis*- and *trans*-β-chlorovinyl aldehydes[15], seem to be applicable. These solvation models result in a shielding effect for R_4 and little or no effect for R_2 in

Table 4. NMR solvent shifts of



No.	R_1	R_2	R_3	R_4	Isomer	Δ in ppm, of -H_1,-CH_2- or -CH_3 [b] R_1	R_2	R_3	R_4	Solvent shift	Solvation model
25[a]	H	Me	Me	Cl	*cis*		0·20	0·40	—	CCl_4-C_6D_6	1b
5[a]	H	Me	Cl	Me	*trans*		0·05	—	0·44	CCl_4-C_6D_6	1a
2					*trans*		0·03			$CDCl_3$ → C_6D_6	1a
4	Me	Me	Cl	H	*trans*		0·15	—	0·65	$CDCl_3$-C_6D_6	1a
7	Ph	Me	Cl	H	*trans*		0·12	—	0·37	$CDCl_3$-C_6D_6	1a
18	Ph	H	Me	Cl	*cis*		0·40	0·47	—	$CDCl_3$-C_6D_6	1c
20	Ph	H	Et	Cl	*cis*		0·44	0·46	—	$CDCl_3$-C_6D_6	1c
22	Me	H	Me	Cl	*cis*		0·39	0·46	—	$CDCl_3$-C_6D_6	1c
19	Ph	H	Cl	Me	*trans*		0·15	—	0·15	$CDCl_3$-C_6D_6	1d
6	Ph	H	Cl	Et	*trans*		0·17	—	0·06	$CDCl_3$-C_6D_6	1d
3	Me	H	Cl	Me	*trans*		0·31	—	0·15	$CDCl_3$-C_6D_6	1d
1					*trans*			—	0·04	$CDCl_3$-C_6D_6	1d

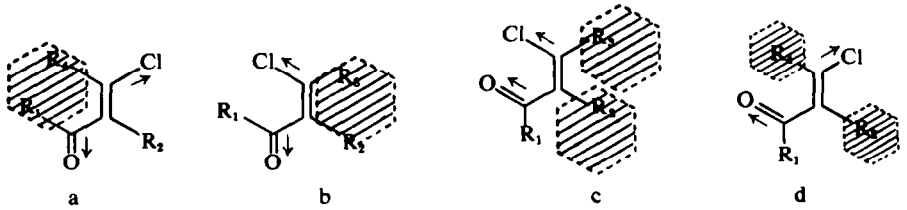
[a] From Ref 15. The solvent shifts are obtained by only a partial replacement of CCl_4 by C_6D_6.
[b] $\Delta = \delta_{CDCl_3} - \delta_{C_6D_6}$.

the case of *trans*-β-chlorovinyl ketones (Fig 1a), and a shielding effect for R_2 and R_3 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.

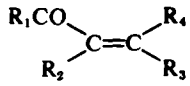
Contrary, in 1d the dipoles are not parallel and the solvating benzene molecules are prevented from a close approach by the chlorine and oxygen atoms, the negative ends of the dipoles. As a result only small solvent shifts can be expected. The solvation models for *cis*- and *trans*-β-chlorovinyl ketones 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 R_1 and R_2 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*-β-chlorovinyl ketones



a b c d

Fig 1.

Table 5. NMR solvent shifts of



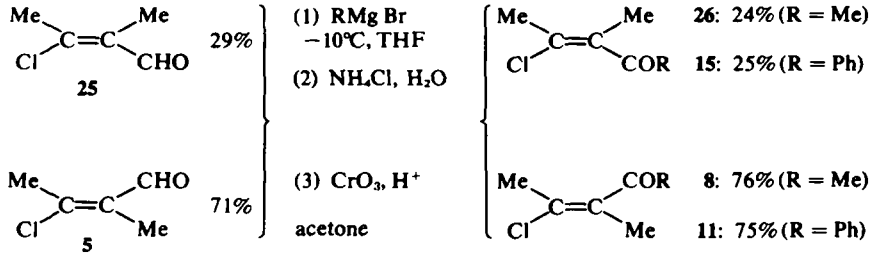
No	R_1	R_2	R_3	R_4	Isomer	Δ in ppm of $-CH_2$-or-CH_3 R_2	R_3	R_4	Solvent shift	Solvation model
26	Me	Me	Me	Cl	*cis*	0·66	0·66	—	$CDCl_3$-C_6D_6	1c
34	CH_2Cl	Me	Me	Cl	*cis*	0·34	0·41	—	$CDCl_3$-C_6D_6	1c
35	$CHCl_2$	Me	Me	Cl		0·23	0·31	—	$CDCl_3$-C_6D_6	1c
27	Me	Et	Et	Cl	*cis*	0·41	0·47	—	$CDCl_3$-C_6D_6	1c
15	Ph	Me	Me	Cl	*cis*	0·39	0·50	—	$CDCl_3$-C_6D_6	1a-1c
28	Ph	Et	Et	Cl	*cis*	0·27	0·38	—	$CDCl_3$-C_6D_6	1a-1c
13	Ph	$-(CH_2)_4-$		Cl	*cis*	=C-CH_2-CH_2 0·30	0·46	—	$CDCl_3$-C_6D_6	1a-1c
8	Me	Me	Cl	Me	*trans*	0·28	—	0·15	$CDCl_3$-C_6D_6	1d
9	Me	Et	Cl	Et	*trans*	0·15		0·07	$CDCl_3$-C_6H_6	1d
32[a]	Me	Me	Me	Me	—	0·40	0·19	0·02	CCl_4-C_6H_6	
11	Ph	Me	Cl	Me	*trans*	0·21	—	0·11	$CDCl_3$-C_6D_6	1b-1d
29	Ph	Et	Cl	Et	*trans*	0·10	—	0·04	$CDCl_3$-C_6D_6	1b-1d
33	Ph	Me	Me	Me	—	0·13	0·28	0·11	$CDCl_3$-C_6D_6	

[a] The solvent shifts denoted have been calculated from the NMR data of ref 10 in CCl_4 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, Timmons[11] 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 R_2 and R_3 and small or negative shifts for R_4, while S-*trans* conformations give large solvent shifts for R_3, relatively large solvent shifts for R_4 and a small one for R_2. 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 *cis*-alkyl 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 R_3 (0·31–0·66 ppm), than the *trans* isomers (0·04–0·15 ppm) for R_4.

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* proportion[15], 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*-β-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 CCl_4-C_6H_6(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 $\epsilon = \frac{\log_{10}(T°/T)}{cl}$, c = concentration in mol l^{-1}, l = the cell path length in cm. The apparent integrated intensity was calculated from $E = K \Delta\nu_{\frac{1}{2}} . \epsilon$, where $\Delta\nu_{\frac{1}{2}}$ 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-cyclohexanone[17] (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 Hall[18] from 2-methyl-1, 3-cyclohexanedione, with PCl_5. The product was purified by distillation on a "Kugel-rohr" (oventemperature 135°, 30 mm Hg).

β-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 $AlCl_3$ catalysed addition of acid chlorides to acetylenes. Acid chloride (0·01 mole) and $AlCl_3$ (0·01 mole) in 25 ml dry dichloromethane were stirred at room temp until all the $AlCl_3$ 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 $AlCl_3$-complex was decomposed with a mixture of ice HCl 10%. The organic layer was washed successively with water, $NaHCO_3$ aq and water. After drying on anhyd $MgSO_4$ 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_4-C_6H_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-butanone[19]. 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% **22**, no further purification
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 diëthylcyclopentenone
11 + 15	100°, 0·8 mm	(b): pure **11** and a mixture of **15** and the yellow 2,3 dimethyl indenone, which was separated by method (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 separation.
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 procedure[15], 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 2-chloro-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. NH_4Cl aq, as described[21]. The resulting product was distilled under vacuum (155°, 1 mm): 52·5 g (yield 84%). This benzylic alcohol was dissolved in 150 ml acetone and 60 ml Jones reagent[22] 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 HCO_3 aq, water and then dried on anhyd $MgSO_4$ 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-enal[15] (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 $AlCl_3$ 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 Chambion[23]. The product was distilled under vacuum (140°, 18 mm). A chromatographic separation on a silicagel thinlayer with CCl_4-C_6H_6(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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