cyclopentadiene which was added over a few minutes. The temperature was maintained at 0 to −7°.

Precipitation of the product usually occurred within 1 hr. The mixture was stirred for an additional hour, after which the product was filtered off giving 20 g (95%) of dimethanol **67**: mp 120–123°. Nmr analysis indicated an isomeric mixture of **67a** and **b** with the symmetrical isomer **67a** predominating by a ratio of 3:1. Repeated recrystallization from methylene chloride eventually raised the melting point to 133–135°. By nmr analysis, this material was almost pure α,α,α′,α′-tetra-2-pyridyl-1,3-cyclopentadiene-1,4-dimethanol, *i.e.*, the symmetrical isomer **67a**.

The nmr spectrum of **67a** ($CDCl_3$) exhibited a triplet centered at δ 6.00 (vinyl protons), a triplet centered at δ 3.18 (methylene protons), and a series of multiplets ranging from δ 6.9 to 8.55 aromatic protons) with integrated intensities of 2:2:16, respectively.

Characterization was done on a mixture of the two isomers (**67a** and **b**): $\lambda_{max}^{CHCl_3}$ 3.0, 6.32, 6.40 μ; λ_{max}^{MeOH} 262 (ε 20,800), 267 (sh) mμ (18,300).

Anal. Calcd for $C_{27}H_{22}N_4O_2$: C, 74.63; H, 5.10; N, 12.90. Found: C, 74.57; H, 5.21; N, 12.77.

The nmr spectrum ($CDCl_3$) of the mixture of **67a** and **b** showed two quartets at δ 5.90 and 6.22 (vinyl protons of unsymmetrical isomer **67b**), a triplet centered at δ 6.00 (vinyl protons of symmetrical isomer **67a**), a triplet centered at δ 3.18 (methylene protons of **67a**), and a triplet at δ 3.13 (methylene protons of **67b**).

1,4-Bis(α-hydroxy-α,α-di-2-pyridylmethyl)-5-norbornene-2,3-dicarboximide (68a, b).—A solution of 5 g (0.012 mole) of the isomeric mixture of diols **67a** and **b** and 1.1 g (0.012 mole) of maleimide in 25 ml of benzene was heated under reflux for 4 hr. The filtered product weighed 3.1 g (51%): mp 240° dec. One recrystallization from dimethylformamide–water solution gave white crystalline isomer **68a**: mp 240° dec; λ_{max}^{KBr} 3.04, 5.65, 5.86, 6.32, 6.40 μ; λ_{max}^{MeOH} 255 (sh) (ε 12,900), 260 (14,200), 266 (sh), mμ (10,900).

Anal. Calcd for $C_{31}H_{25}N_5O_4$: C, 70.04; H, 4.74; N, 13.18. Found: C, 69.81; H, 4.94; N, 12.95.

The benzene mother liquors of the first crop slowly deposited additional crystalline material which was extracted with boiling benzene. Filtration removed the less soluble **68a** and cooling of the filtrate gave white crystals. One recrystallization from benzene gave crystalline isomer **68b**: mp 155–160°.

Anal. Found: N, 12.88.

Tlc (silica gel, cyclohexane–ethylacetate–methanol, 6:4:1) showed isomer **68b** running faster than **68a**.

The nmr spectrum ($CDCl_3$) of isomer **68a** showed resonance peaks at δ 6.63 (sharp singlet, 5,6-vinyl protons), δ 3.72 (sharp singlet, 2,3-protons), and δ 2.05 (AB quartet, 7-protons). The proton integration ratio was 2:2:2.

The nmr spectrum ($CDCl_3$) of isomer **68b** showed resonance peaks at δ 6.57 (sharp singlet, 6-vinyl proton), δ 3.75 (multiplet, 4-proton), δ 3.25 (multiplet, 2,3-protons), and δ 1.83 (unresolved AB pattern, 7-protons). The proton integration ratio was 1:1:2:2.

Acknowledgment.—We wish to thank Dr. Harold Almond for his aid in the interpretation of the nmr spectra, Mr. James Plampin and Mr. Michael J. Zelesko for the synthesis of several compounds, and Mrs. M. C. Christie for many of the analytical and spectral results.

Vibrational Spectra and Structure of Substituted Unsaturated Carbonyl Compounds. IV. Infrared and Raman Spectra of Methyl β-Chlorovinyl Ketone and Its Deuterated Derivatives

Janusz Dąbrowski and Jacek Terpiński

Institute of Organic Chemistry, Polish Academy of Sciences, and Department of Organic Chemistry,
Institute of Technology, Warsaw, Poland

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Infrared and Raman spectra revealed that the title compounds exist in two conformational forms: *s-cis* and *s-trans*. A number of bands due to those forms have been assigned.

Infrared spectra of various β-substituted α,β-unsaturated ketones are characterized by considerable displacement of the $\nu_{C=O}$ and $\nu_{C=C}$ absorption bands to lower frequencies[1-6] resulting from equalization of the single and double bonds in the mesomeric system O=C—C=C—X. Consequently, the remaining stretching skeletal vibrations of this system are expected to shift to higher frequencies.[2] These vibrations, however, appear in the fingerprint region and there are serious difficulties with their assignment. Further complications may arise in connection with rotational isomerism and Fermi resonance which may increase the number of absorption bands to be assigned. This is presumably the cause why most interpretations are restructed to the 1500–1700-cm^{-1} spectral region. For this reason, it is important to obtain more spectral information on substituted unsaturated carbonyl compounds which play an important role both in spectroscopy[6] and in organic chemistry.

In the present investigation methyl β-chlorovinyl ketone (I) was studied. This compound has the advantage of showing a relatively simple infrared spectrum thus enabling to assign most of the essential frequencies with a high degree of certainty. The interpretation is based on comparisons with infrared spectra of three differently deuterated methyl β-chlorovinyl ketones (II–IV) and with Raman spectra of two of them (I and III). (See Figures 1–6.) The assignment thus derived may be of value in many other cases since compounds I–IV are related to various unsaturated ketones.

$$\underset{\text{I}}{{}^4CH_3{}^3CO{}^2CH{=}{}^1CH{-}Cl} \qquad \underset{\text{II}}{CD_3COCH{=}CH{-}Cl}$$

$$\underset{\text{III}}{CH_3COCD{=}CD{-}Cl} \qquad \underset{\text{IV}}{CD_3COCD{=}CD{-}Cl}$$

Recently Benson and Pohland[7] reported the $\nu_{C=O}$, $\nu_{C=C}$, vinyl γ_{C-H}, and ν_{C-Cl} frequencies of methyl β-chlorovinyl ketone and a series of its homologs; however, the resolution of the apparatus used was ap-

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(1) N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank, and D. J. Wallace, *J. Am. Chem. Soc.*, **71**, 3337 (1949).

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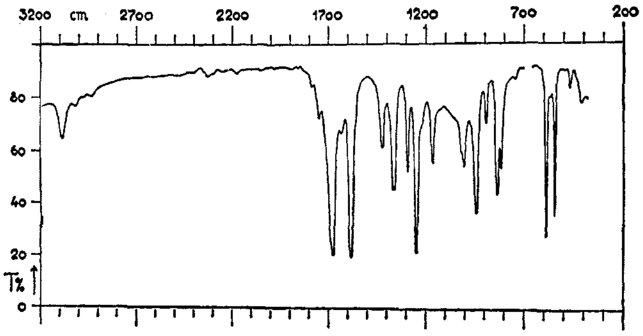

Figure 1.—Infrared spectrum (film) of $CH_3COCH{=}CHCl$ (I).

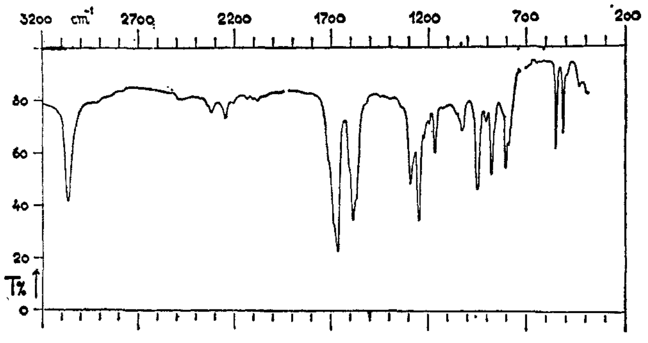

Figure 2.—Infrared spectrum (film) of $CD_3COCH{=}CHCl$ (II).

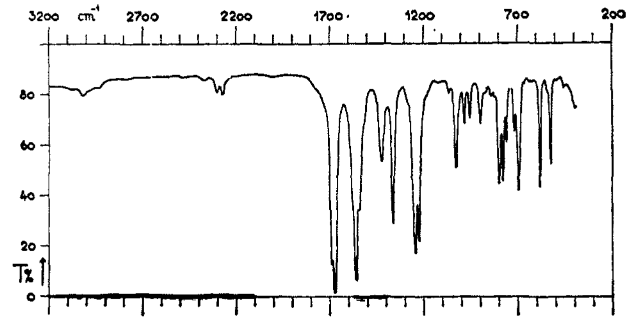

Figure 3.—Infrared spectrum (film) of $CH_3COCD{=}CDCl$ (III).

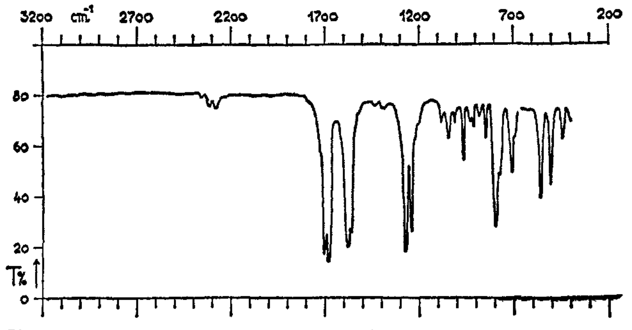

Figure 4.—Infrared spectrum (film) of $CD_3COCD{=}CDCl$ (IV).

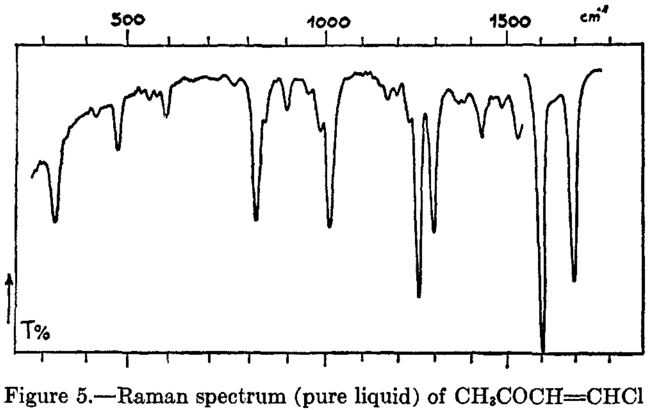

Figure 5.—Raman spectrum (pure liquid) of $CH_3COCH{=}CHCl$ (I).

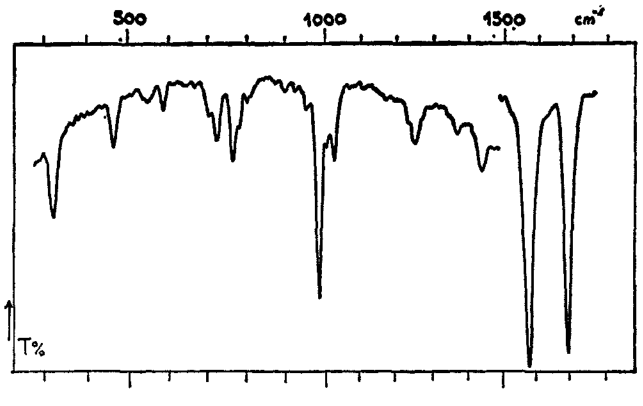

Figure 6.—Raman spectrum (pure liquid) of $CH_3COCD{=}CDCl$ (III).

parently unsufficient to enable detection of bands splittings which, as will be shown below, are due to rotational isomerism of β-chlorovinyl ketones.

Results and Discussion

The infrared absorption bands, the Raman bands, and the corresponding assignment are given in Table I.

The absorption band due to the vinyl C–D stretching vibration in III is split into two components of equal intensity. Whether this splitting is connected with symmetrical and asymmetrical vibration or, rather, with rotational isomerism could not be ascertained. In any case the corresponding band of the C–H vibration shows no sign of splitting, which, however, may be due to lower resolution in this part of the spectrum.

The $\nu_{C=O}$ and $\nu_{C=C}$ bands are asymmetrically broadened or even split in the spectra of pure liquids and clearly split in those of solutions (Figure 7). Theoretically, this broadening or splitting may be caused by various factors such as association, Fermi resonance, and *cis–trans* and rotational isomerism. It will be shown in a following paper of this series[8] that association does not play any marked role in this effect. Fermi resonance would require the coincidence of too many factors since a number of other bands discussed below are also split. As to *cis–trans* isomerism, Benson and Pohland[7] showed by nmr measurements that methyl β-chlorovinyl ketone exists to at least 95% in the *trans* form, and the "additional" infrared absorptions are too strong to be caused by small admixtures of the *cis* form. This elimination leaves the rotational isomerism as the most probable cause of observed bands splittings.

As the coplanar arrangement of the C═O and C═C groups is energetically favored only plane rotational isomers, *viz.*, the *s-cis* and *s-trans* ones, are expected. However, according to Stuart–Briegleb atomic models the completely plane *s-trans* conformation is hardly possible on account of the repulsion between methyl and β-vinyl hydrogen (or deuterium). On the other hand, this repulsion ceases to play any marked role at dihedral angles between C═O and C═C groups only slightly different from 180°, which means that the loss of the resonance energy is rather unessential and the slightly twisted "quasi-*s-trans*" form[9] is energetically comparable with the strain-free plane *s-cis* one. Our

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[8] J. Dabrowski and K. Kamienska-Trela, in press.

[9] Further called *s-trans*.

TABLE I

VIBRATIONAL BANDS (IN WAVENUMBERS) AND THEIR ASSIGNMENT TO VIBRATIONAL MODES OF METHYL β-CHLOROVINYL KETONES

I ($CH_3COCH{=}CHCl$)				II ($CD_3COCH{=}CHCl$)		III ($CH_3COCD{=}CDCl$)				IV ($CD_3COCD{=}CDCl$)	
Infrared, cm^{-1}	Raman, cm^{-1}	ρ	Assignment	Infrared, cm^{-1}	Assignment	Infrared, cm^{-1}	Raman, cm^{-7}	ρ	Assignment	Infrared, cm^{-1}	Assignment
...	319 (m)					...	315 (m)	0.43			
414 (w)	419 (vw)	...		436 (w)		398 (w)	...			430 (w)	δ_{C-Cl} ?
470 (w)	471 (m)	0.24	δ_{C-Cl} ?	498 (vw)	δ_{C-Cl} ?	456 (vw)	457 (m)	0.30	δ_{C-Cl} ?	497 (m)	$\gamma_{C=O}$?
548 (s)	536 (vw)	...	$\gamma_{C=O}$?	517 (m)	$\gamma_{C=O}$?	528 (s) :	...		$\gamma_{C=O}$?	544 (m)	$\gamma_{C=O}$?
566 (w)	...			549 (m)	$\gamma_{C=O}$?	541 (vw)	545 (vw)	0.54		689 (m)	
589 (s)	587 (w)	0.26	$\gamma_{C=O}$?	728 (w)		582 (s)	583 (w)	0.29	$\gamma_{C=O}$?	705 (s)	$\gamma_{=C-D}$
747 (vw)	759 (vw)	...		760 (vw)		693 (s)	699 (w)	...	$\gamma_{=C-D}$	755 (m)	
821 (s)	815 (s)	0.60	$\nu_{C-Cl}{}^{a}$	790 (s)	$\nu_{C-Cl}{}^{a}$	719 (m)	717 (m)	0.84		778 (m)	$\nu_{C-Cl}{}^{a,c}$
840 (s)	834 (m)	0.84	$\nu_{C-Cl}{}^{b}$	805 (s)	$\nu_{C-Cl}{}^{b}$	755 (m)	759 (m)	0.74		786 (s)	ν_{C-Cl} b^{b,c}
894 (m)	897 (w)	0.84	ν_{C-C} ?	876 (vs)		774 (s)	775 (m)	0.82	$\nu_{C-Cl}{}^{a}$	840 (w)	
945 (vs)	945 (vw)	0.33	$\gamma_{=C-H}$	905 (m)	ν_{C-C} ?	792 (s)	799 (w)	0.84	$\nu_{C-Cl}{}^{b}$	880 (vw)	
...	981 (m)	0.33		943 (vs)	$\gamma_{=C-H}$	838 (vw)	...			905 (w)	ν_{C-C} ?
1006 (s)	1009 (s)	0.40	ρ_{CH_3} ?	1030 (m)	δ_{CD_3} *sym*	871 (vw)	...			920 (vw)	ρ_{CD_3} ?
1020 (sh)	...			1062 (w)	δ_{CD_3} *as*	895 (m)	897 (vw)	...	ν_{C-Cl} ?	956 (m)	$\delta_{=C-D}$
1164 (s)	1162 (w)	...	$\nu_{C-C}{}^{a}$	1137 (vw)		952 (m)	954 (w)	0.36	$\delta_{=C-D}$	1000 (vw)	
...	1185 (vw)	...		1171 (s)	$\nu_{C-C}{}^{a}$	983 (m)	984 (vs)	0.23		1036 (m)	δ_{CD_3} *sym*
1225 (sh)	1220 (w)	0.38		1202 (m)		...	1000 (m)	...		1070 (w)	δ_{CD_3} *as*
1246 (vs)	1247 (vs)	0.35	$\nu_{C-C}{}^{b}$	1226 (m)		1030 (s)	1025 (m)	0.32	ρ_{CH_3} ?	1193 (w)	
1290 (s)	1292 (vs)	0.29	$\delta_{=C-H}$	1252 (vs)	$\nu_{C-C}{}^{b}$	1226 (vs)	1220 (sh)	...	$\nu_{C-C}{}^{a}$	1215 (m)	
1360 (s)	1361 (vw)	...	δ_{CH_3} *sym*	1293 (vs)	$\delta_{=C-H}$	1246 (vs)	1247 (m)	0.29	$\nu_{C-C}{}^{b}$	1235 (vs)	$\nu_{C-C}{}^{a}$
1369 (s)	1369 (vw)	...				1361 (vs)	1360 (vw)	0.75	δ_{CH_3} *sym*	1266 (vs)	$\nu_{C-C}{}^{b}$
1424 (m)	1424 (m)	0.68	δ_{CH_3} *as*			1424 (s)	1427 (m)	0.80	δ_{CH_3} *as*		
...	1530 (m)	0.36	?								
1585 (vs)	1587 (vs)	0.31	$\nu_{C=C}{}^{a}$	1571 (sh)	?	1545 (s)	...		?	1555 (vs)	?
1631 (m)	...		$2\nu_{C-Cl}$?	1586 (vs)	$\nu_{C=C}{}^{a}$	1563 (vs)	1558 (vs)	0.32	$\nu_{C=C}{}^{a}$	1571 (vs)	$\nu_{C=C}{}^{a}$
1677 (vs)	1678 (vs)	0.36	$\nu_{C=O}{}^{b}$	1666 (vs)	$\nu_{C=O}{}^{b}$	1675 (vs)	1672 (vs)	0.39	$\nu_{C=O}{}^{b}$	1668 (vs)	$\nu_{C=O}{}^{b}$
1691 (sh)	...	...	$\nu_{C=O}{}^{a}$	1690 (sh)	$\nu_{C=O}{}^{a}$	1690 (vs)	...		$\nu_{C=O}{}^{a}$	1690 (vs)	$\nu_{C=O}{}^{a}$
1755 (w)	...	...				2275 (w)	...		$\nu_{=C-D}$		
2938 (w)			ν_{C-H} *sym*	2250 (vw)	ν_{C-D}	2305 (w)	2300 (s)	0.45		2270 (w)	ν_{C-D}
3023 (w)			ν_{C-H} *as*	2331 (vw)		2998 (vw)	...		ν_{C-H} *sym*	2310 (w)	
3090 (m)			$\nu_{=C-H}$	3079 (m)	$\nu_{=C-H}$	3010 (w)			ν_{C-H} *as*	2360 (vw)	?

[a] *s-cis* conformation. [b] *s*-trans conformation. [c] Split in solutions only.

conclusions contradict the view expressed by Benson and Pohland,[7] who supposed chlorovinyl ketones to exist entirely in the *s-trans* form. These authors used the Dreiding models which are not so suitable for observing repulsion effects as the Stuart–Briegleb ones.

It should be noted that similar band splittings were observed by several authors[10,11] in vibrational spectra of *unsubstituted* α,β-unsaturated ketones and also attributed to the occurrence of two conformational isomers. When four bands were observed the higher of the two C=O bands and the lower of the C=C bands were ascribed[10,11] to the *s-cis* form while the two inner bands were assigned to the *s-trans* form. The relative intensities of the observed bands are very distinctive. Whereas the *cis*-C=O band weakens in Raman the *trans*-C=O grows up. The *cis*-C=C gets stronger in Raman and the *trans*-C=C is weak both in infrared and Raman spectra. Noack and Jones[11] suggested that these seeming irregularities in bands intensities might be due to partial coupling of the C=O and C=C stretching modes and this idea was further developed by Sobolev and Aleksanyan.[12] Considering the possible forms of vibrations, these authors reasonably concluded that the in-phase stretching mode is expected to give more strong Raman and infrared bands as compared with the out-of-phase vibration since both the polarity and polarizability of the system change more in the former case. To bring the experimentally observed intensities into accordance with this idea Sobolev and Aleksanyan postulated a reverse assignment of the in-phase and out-of-phase vibrations in the *s-cis* and *s-trans* forms; *viz.*, ν_s (*i.e.*, $\approx \nu_{C=O}$) > ν_{as} (*i.e.*, $\approx \nu_{C=C}$) in the *trans* form and ν_s (*i.e.*, $\approx \nu_{C=C}$) < ν_{as} (*i.e.*, $\approx \nu_{C=O}$) in the *cis* form. The above scheme was successfully employed also to conjugated *s-cis* and *s-trans* dienes.[13]

The same pattern can be employed to the double-bond absorption region of the spectra of compounds I–IV shown on Figure 7. Band A, which is much weaker in the Raman, is ascribed here to the C=O vibration of the *s-cis* form and band B, strong both in Raman and infrared spectra, to the same mode of the *s-trans* one. The band C, strong in infrared and stronger in Raman, is assigned to the C=C *s-cis* band (however, see the discussion below on passible overlapping with C=C *s-trans* band).

The intensities of bands A and C increase in spectra of solutions in nonpolar solvents (hexane, carbon tetra-

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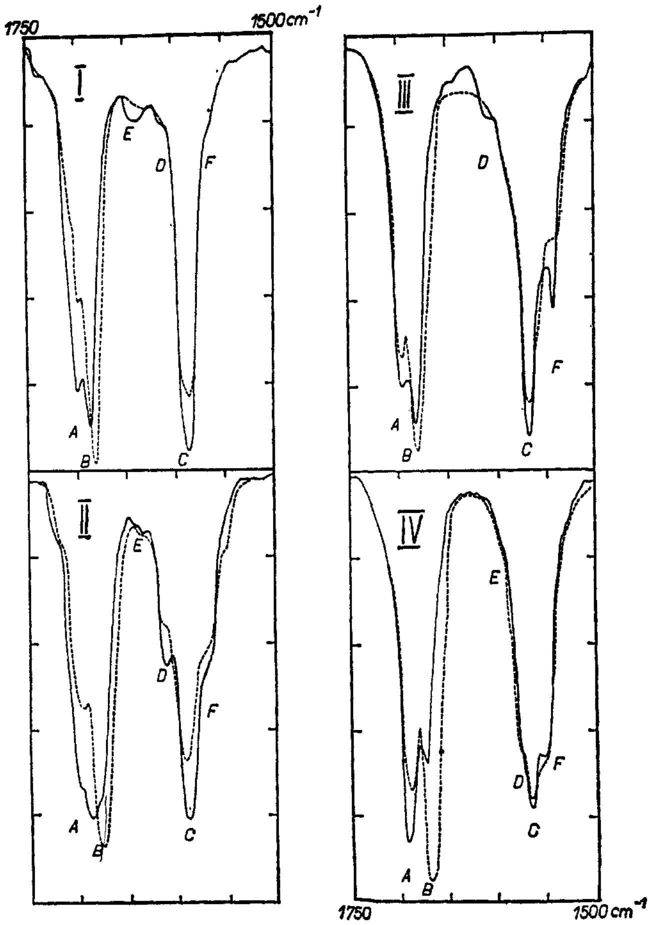

Figure 7.—The 1750–1500-cm^{-1} region of the infrared spectra of compounds I–IV in tetrachloroethylene (———) and in acetonitrile (- - - -): concentration, 0.5 *M*; cell thickness, 0.1 mm.

chloride, and tetrachloroethylene), thus confirming their assignment to the same conformational isomer (*s-cis*), whereas band B grows more intense in polar solvents (acetonitrile and methanol). That means that the equilibrium *s-cis* ⇄ *s-trans* shifts toward the *s-trans* form with increasing polarity of the solvent. This clear result will be utilized when assigning the ν_{C-Cl} and ν_{C-C} bands of the two rotational isomers (see below).

In this spectral region several other bands occur but none of them could be ascribed with certitude to the $\nu_{C=C}$ vibration of the *s-trans* conformer. In general,[10,11] this band appears at higher frequency and is weaker than that of the *s-cis* form. Band D fulfills these requirements but, on the other hand, shows reverse intensity changes compared with band B (*i.e.*, C=O *s-trans*) when varying the polarity of the solvent; it is therefore probably due to another vibration—possibly to an overtone of the C–Cl stretch. The same assignment can be tentatively given to band E.

The origin of band F is not clear. It appears at a frequency too low to be ascribed to the C=C band and shows no appreciable solvent effect. A similar band was observed by Noack and Jones[11] in vinyl ketones and was attributed to a combination vibration.

It should be added that no distinct band corresponding to the $\nu_{C=C}$ vibration of the *s-trans* form could be observed in different unsubstituted[10,11] and amino-substituted[5] vinyl ketones. Taking all these facts into account, we are inclined to assume that, similarly to what was observed for other vinyl ketones,[5,10,11] the C=C *s-trans* band is overlapped by the stronger *s-cis* band.

The CH_3 bending frequencies of I (1424, 1369, and 1360 cm.$^{-1}$) and III (1424 and 1360 cm^{-1}) are readily recognizable since the corresponding bands disappear completely from the spectra of CD_3 derivatives II and IV. The CD_3 bending vibrations give rise to bands at 1062 and 1030 cm^{-1} in II and at 1070 and 1036 cm^{-1} in IV showing almost exactly the expected isotopic shift.

There are only few data in the literature on the in-plane bending mode of the olefinic protons and deuterons in *trans*-disubstituted olefins. Our results permit to fix these vibrations with certainty at 1290 cm^{-1}

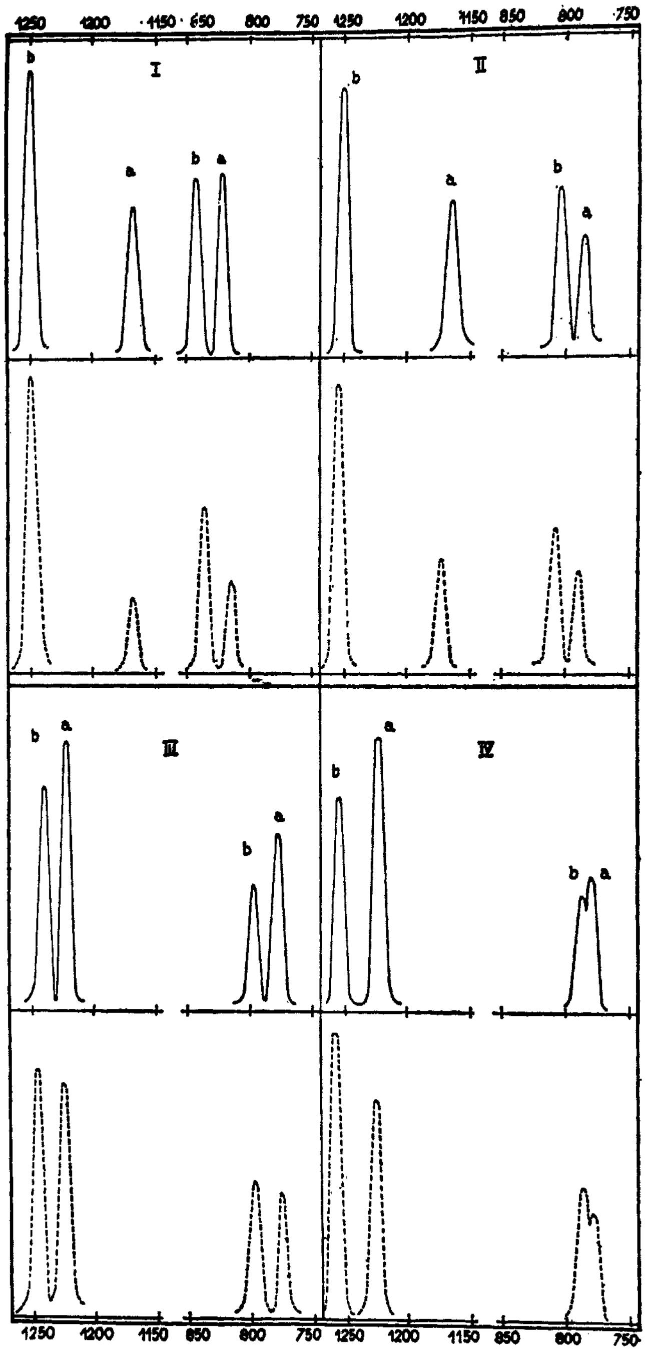

Figure 8.—Relative intensities of C–C and C–Cl bands of the *s-cis* (a) and *s-trans* (b) conformers of compounds I–IV in nonpolar solvent (———, hexane) and in polar solvent (- - - -, acetonitrile): concentration, 0.5 *M*; cell thickness, 0.1 mm.

(I) for C–H and 952 cm^{-1} (III) for C–D groups. The band of the corresponding out-of-plane vibrations appears at 945 (I) and 693 cm^{-1} (III). The observed isotopic shifts of these bands are in good agreement with the theoretical value. According to expectation the bands due to vinyl γ_{C-H} and γ_{C-D} vibrations are stronger than those of the δ_{C-H} and δ_{C-D} modes in the infrared spectra, whereas in the Raman spectra the contrary is true.

For the C–Cl stretching mode in compound I, Benson and Pohland proposed the value 842 cm^{-1}. The position of this particular band is in agreement with our results. However, there is another strong infrared band at 821 cm^{-1} which can also be ascribed to the C–Cl stretching vibration. The assignment of these two bands to the particular conformational isomers follows from their intensity changes in different solvents: the enhancement of the lower band (821 cm^{-1}) in hexane solution, compared with solution in acetonitrile, suggests it to correspond to the *s-cis* form (see the above discussion on *s-cis–s-trans* equilibrium). Consequently, we ascribe the upper band (842 cm^{-1}) to the quasi-*s-trans* form. Additional support for the above assignment is provided by measuring the depolarization ratios of these bands: that of the nonplanar quasi-*s-trans* form lacking symmetry is not polarized ($\rho = 0.84$), while that of the planar *s-cis* form is partly polarized ($\rho = 0.60$).

It may be concluded that the C–Cl stretching vibration is not characteristic since ρ exceeds in both cases the maximum value (0.5) for characteristic vibrations of diatomic fragments.[14] This conclusion is in agreement with the displacement of both the C–Cl bands to lower frequencies occurring upon substituting the vinyl hydrogens by deuteriums (see Table I), which gives evidence for a strong mechanical coupling. A similar effect concerning the C–Cl vibrations was observed with acetyl chloride and its deuterated analogs.[15]

There remain four intense infrared bands of compound I in the NaCl spectral region to be assigned, *viz.*, those at 1246 (vs), 1164 (s), and 1005 (s) cm^{-1} with a shoulder at 1020 and 894 (m) cm^{-1}. Taking into account that the first two of these bands occur in all spectra I–IV and that the lower of them intensifies in nonpolar solvents (Figure 8) we assign them to the C–C stretching vibration of the system O=C—C=C—Cl in the quasi-*s-trans* and *s-cis* form, respectively. The 1020- and 1005-cm^{-1} frequencies are probably due to the CH_3 rocking mode in those two conformational isomers. The band at about 900 cm^{-1} occurring in all spectra (I–IV) can be tentatively assigned to the C-3–C-4 stretching mode.

It seems impossible to assign the bands of the KBr region unless theoretical calculations are made. Still, it may be assumed that two of the strong infrared bands in the 500–600-cm^{-1} range are due to the C=O out-of-plane bending mode in the two conformers (see Table I).

The remaining assignment for the deuterated compounds II–IV are given in Table I.

It should be added that no marked intensity changes were observed[8] when measuring, within the temperature range 20–150°, the spectra of chloro- and iodovinyl ketones which reveal similar bands splitting. This means that the energy of the two conformers is of comparable value.

Experimental Section

Deuterioacetylene, DC≡CD, was generated by dropping D_2O into calcium carbide and purified by passing it through H_2SO_4.

Deuterioacetic acid, CD_3COOD, was obtained by decarboxylation of deuteriomalonic acid derived from carbon suboxide and deuterium oxide as described by Wilson.[16] Its isotopic purity was controlled spectroscopically.

Deuterioacetyl chloride, CD_3COCl, was prepared from CD_3COOD and PCl_3 in the presence of 20 mole % of $ZnCl_2$.[17]

Chlorovinyl Ketones.—All substances were obtained according to standard methods[7,18] from appropriate acetyl chloride and acetylene in CCl_4 as solvent and purified by threefold distillation. **Methyl β-chlorovinyl ketone (I)**, $CH_3COCH{=}CH{-}Cl$, had bp 54–55° (40 mm), $n^{25}D$ 1.4654. **Methyl β-chloro-α,β-dideuteriovinyl ketone (III)**, $CH_3COCD{=}CD{-}Cl$, had bp 54–55° (40 mm), $n^{25}D$ 1.4651. **Trideuteriomethyl β-chlorovinyl ketone (II)**,[19] $CD_3COCH{=}CH{-}Cl$, had bp 54–55° (40 mm), $n^{25}D$ 1.4641. **Methyl β-chlorovinyl-d_5 ketone (IV)**,[19] $CD_3COCD{=}CD{-}Cl$, had bp 55–56° (40 mm), $n^{25}D$ 1.4625.

Measurements.—Infrared spectra were recorded with a Hilger-, $n^{25}D$ 1.4641. 800 spectrometer with sodium chloride and potassium bromide optics.

Raman spectra of pure liquids were recorded with a Hilger & Watts spectrograph E-612 with direct recording equipment; slit width 0.15 mm.

The depolarization ratios of Raman lines were determined with the use of "Polaroid" sheets.[20]

Indene, polystyrene, 1,2,4-trichlorobenzene, and toluene were used for instrument calibrations and the reported wavenumbers are estimated to be within ±1–2 cm^{-1}.

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[19] The reaction product was decomposed with D_2O–ice; otherwise, partial exchange of deuterium from the methyl group for hydrogen occurred.

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