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Vibrational Spectra and Structure of Substituted Unsaturated Carbonyl Compounds. VI. β-Halogeno- and β-Halogenodeuteriovinyl Ketones

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The infrared spectra of several chloro-, bromo- and iodovinyl ketones and their partly deuterated derivatives were investigated in the liquid state and in solutions. A Raman spectrum of one of these substances was also obtained. It has been shown that, unlike enamino- and hydroxyvinyl ketones, the title compounds exhibit fairly characteristic absorption bands due to carbonyl and skeletal vibrations. The splittings observed in the double bond stretching region are accounted for by rotational isomerism. Several assignments of the group frequencies are proposed.

It has been shown that β-amino[1-3] and β-hydroxy substituted α, β-unsaturated ketones[4] are characterized by partial equalization of the double and single bonds causing strong coupling of the C=O and C=C stretching vibrations and very large frequency shifts. On the other hand the carbonyl and vinyl bands of the unsubstituted vinyl ketones are less shifted,[5,6] the corresponding vibrations being practically localized. It is therefore, interesting to investigate unsaturated ketones with substitutents of various types in the β position and compare their spectral characteristics with those obtained in the two extreme cases mentioned.

In the present work halogens were the substituents in the β position. In order to obtain as far as possible detailed assignments, all substituents were systematically varied (R–CO–CR′=CR′–X; R= CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7 or *t*-C_4H_9; R′=H or D; X=Cl, Br or I) The. $\nu_{C=O}$ and $\nu_{C=C}$ vibrations were found to be practically localized and characteristic. Moreover, a number of vibrations in the fingerprint region are also fairly characteristic as could be established by comparison of the spectra of related compounds; this is particularly distinct in the case of β-chloro, bromo and iodo derivatives of ethyl vinyl ketone (compounds IV, VI and VII, Fig. 1) where large parts of the spectra are almost true copies of each other.

Of particular interest are the band splittings observed within the 1500—1700 cm^{-1} region which have been shown in this study to be caused by rotational isomerism.

Recently a number of β-chlorovinyl ketones were spectroscopically investigated by Benson and Pohland[7]; as already pointed out[8] the resolving power of the apparatus used by these authors must have been insufficient and the significant fact of splitting of the absorption bands was overlooked.

A number of infrared and Raman bands of the parent homologue, i. e. methyl-β-chlorovinyl ketone and three of its deuterated derivatives have been assigned in the previous paper of this series.[8]

Experimental

All substances studied in the present work were prepared according to conventional methods. These are listed in Table I. The syntheses of new compounds are described below.

Alkyl-β-chloro-α, β - dideuteriovinyl ketones were synthesized from deuterioacetylene and acyl chlorides similarly as the nondeuteriated chlorovinyl ketones described previously[9] and purified by threefold distillation:

Ethyl-β-chloro-α, β-dideuteriovinyl ketone (V), b. p. 50—51°C/18mmHg, n_D^{25} 1.4586, yield 68.1%;

n-Propyl-β-chloro-α, β-dideuteriovinyl ketone (IX), b. p. 100°C/60 mmHg, n_D^{25} 1.4609, yield 32.0%

Isopropyl-β-chloro-α, β-dideuteriovinyl ketone (XI), b. p. 75—76°C/43 mmHg, n_D^{25} 1.4582, yield 65.0%.

Spectral purity of the deuteriated species was established by the fact that the bands at 3050—3100 cm^{-1} due to C–H vinyl stretch were absent from all spectra of deuteriovinyl compounds while new bands

1) K. Kotera, *Yakugaku Zasshi*, **80**, 1275 (1960).
2) J. Dabrowski, *Spectrochim. Acta*, **19**, 4751 (1963).
3) J. Dabrowski and K. Kamienska-Trela, ibid., **22**, 211 (1966).
4) R. Mecke and E. Funck, *Z. Elektrochem.*, **60**, 1124 (1956).
5) K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2201, 2225 (1961).
6) J. Kossanyi, *Bull. Soc. Chim.*, **1965**, 704.
7) W. R. Benson and A. E. Pohland, *J. Org. Chem.*, **29**, 385 (1964).
8) J. Dabrowski and J. Terpiński, ibid., **31**, 2159 (1966).
9) A. N. Nesmeyanov, N. K. Kochetkov and M. I. Rybinskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1950**, 350.

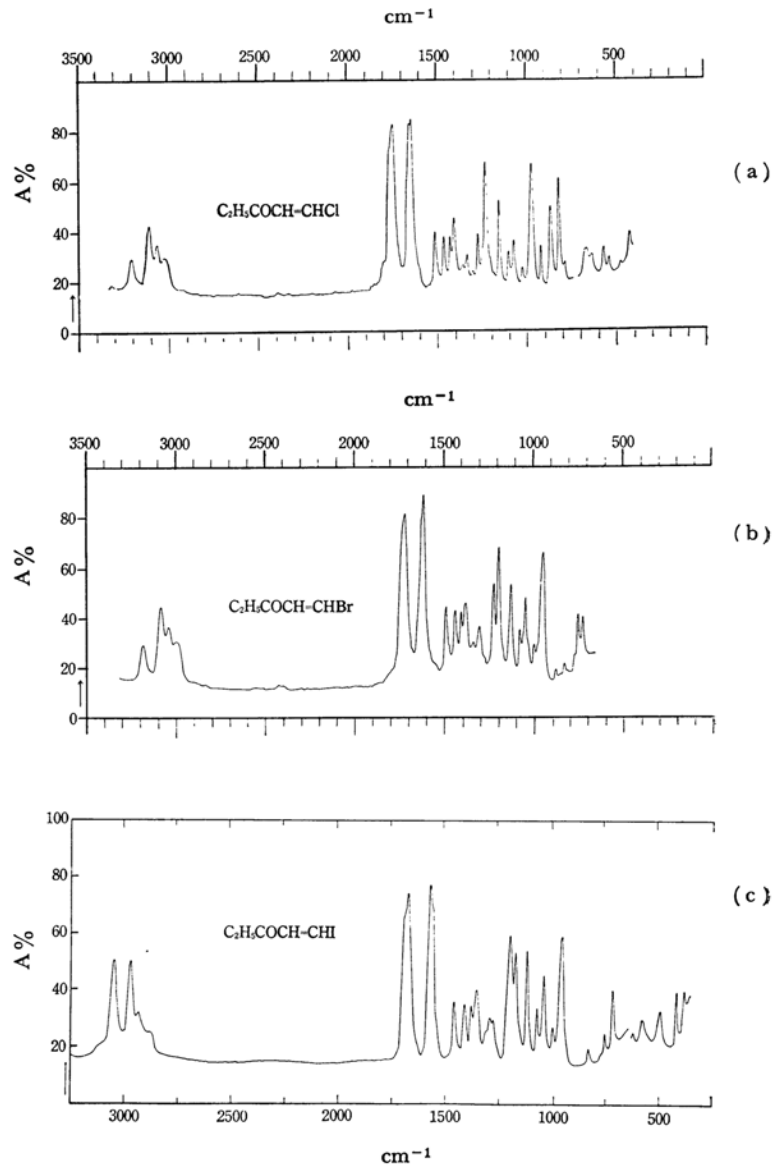


Fig. 1. (a) Infrared spectrum of 1-chloropenten-1-one-3 (IV); neat, liquid film.
(b) Infrared spectrum of 1-bromopenten-1-one-3 (VI); neat, liquid film.
(c) Infrared spectrum of 1-iodopenten-1-one-3 (VII); neat substance; 3250—650 cm^{-1}: melted, film, 650—400 cm^{-1}: crystalline, film.

due to corresponding C–D vibrations arose at 2260—2300 cm^{-1}.

Ethyl-β-bromovinyl ketone (VI) was prepared according to the method described by Niemirowski and coworkers[10] from 4.3 g. (0.0525 mole) of pentyn-1-one-3 and 14 g. of 41% HBr (0.071 mole, water solution). Yield 5.3 g. (62% theor.). Colourless liquid with b. p. 68°C/16 mmHg, n_D^{25} 1.4961.

Found: C, 37.05; H, 4.44; Br, 48.19. Calcd.: C, 36.84; H, 4.33; Br, 49.03%.

Ethyl-β-iodovinyl ketone (VII) was obtained from 5 g. (0.04 mole), ethyl-β-chlorovinyl ketone and 10 g. (0.067 mole) of sodium iodide in acetone solution in the same manner as described by Kochetkov[11] for other homologues. Yield 8.4 g. (60% theor.); white leaflets with m. p. 32—33°C (from pentane).

Found: I, 60.15%. Calcd.: I, 60.42%.

The solvents were purified by the methods used previously.[2] Measurements were carried out using a Hilger H-800 double-beam spectrometer with sodium chloride and potassium bromide optics. Melted substances were investigated in an electrically heated cell and low-melting, crystalline samples in the low-temperature cell described previously.[2] The spectra

10) W. D. Niemirowski, L. F. Czelpanova and A. A. Pietrov, *Zh. Obshch. Khim.*, **31**, 2552 (1961).

11) N. K. Kochetkov, *Dokl. Akad. Nauk SSSR*, **82**, 593 (1952).

TABLE I. WAVE NUMBERS (cm^{-1}) OF THE ABSORPTION BANDS OF β-HALOGENOVINYL KETONES IN THE DOUBLE BOND STRETCHING REGION

Substance and reference to synthesis	Solvent	M mole/l.	Cell thickness mm.	Absorption band A C=O *s-cis*	B C=O *s-trans*	C C=C *s-trans*	D C=C *s-cis*
1	2	3	4	5	6	7	8
$CH_3COCH=CHCl$[9] (I)	—	—	film	1691	1677	1585**	
				1631?			
	C_2Cl_4	0.38	0.06	1697	1686	1583	
$CH_3COCH=CHBr$[10] (II)	—	—	film	1690 sh	1679	1584**	
	C_6H_{12}	0.07	0.28	1707 sh	1691	1586	1581 sh
	CH_3OH	0.63	0.04		1678	1580	
$CH_3COCH=CHI$[11] (III)	—b)		film	1750	1658	1610	1570
				1687			1541
	—c)		film		1675a)	1569a)	
	C_6H_{14}	0.05	0.27	1706	1691	1570	1559 sh
	CH_3OH	0.6	0.04		1671	1566	
$C_2H_5COCH=CHCl$[9] (IV)	—	—	film	1697 sh	1680	1594	1584
	C_6H_{12}	0.09	0.28	1703	1690	1604	1583
	CH_3CN	0.30	0.09	1701	1682	1594	1583
	CH_3OH	0.86	0.04	1704 sh	1679	1593	1585
$C_2H_5COCD=CDCl$ (V)	—	—	film	1691	1681	1564**	
	C_6H_{14}	0.25	0.09	1702	1695	1567	1537?
	CH_3CN	0.24	0.09	1691	1681	1564	
	CH_3OH	1.6	0.02		1680	1562	
$C_2H_5COCH=CHBr$ (VI)	—	—	film	1693 sh	1681	1592 sh	1581
	C_6H_{12}	0.06	0.28	1707	1694	1592 sh	1581
	CH_3OH	0.64	0.04	1685	1679 sh	1592 sh	1582
$C_2H_5COCH=CHI$ (VII)	—b)		film	1686	1656	1576	1564 sh
					1627		
	—c)		film	1691 sh	1681	1575	1562
	C_6H_{12}	0.05	0.28	1704	1691	1576	
	CH_3OH	0.63	0.04		1678	1575	1566 sh
n-$C_3H_7COCH=CHCl$[9]	—	—	film	1689 sh	1679	1587**	
(VIII)	C_6H_{12}	0.07	0.22	1699	1688	1587	
	CH_3OH	0.07	0.04		1673	1586	
n-$C_3H_7COCD=CDCl$ (IX)	—				1683	1563	
	C_2Cl_4	0.13	0.22		1690	1563	
i-$C_3H_7COCH=CHCl$[13] (X)	—		film	1695	1679	1591**	
	C_2Cl_4	0.24	0.06	1699	1684	1590	
	CH_3CN	0.32	0.06	1694	1677	1589	
	CH_3OH	1.10	0.02	1691	1679	1588	
i-$C_3H_7COCD=CDCl$ (XI)	—		film	1690	1683 sh	1560**	
	C_2Cl_4	0.23	0.06	1692	1678 sh	1558	1543 sh
	CH_3OH	0.46	0.02		1676	1557	
$(CH_3)_3CCOCH=CHCl$[14]	—		film	1695		1595	1580 sh*
(XII)	C_2Cl_4	0.07	0.18	1696		1595	1580*
	CH_3OH	0.70	0.04	1690		1592	1579*

* With respect of this band in XII see discussion on p. 2569.
** Overlapping bands of both *s-trans* and *s-cis* forms.
a) Asymetrically broadened, b) Crystalline film, c) Melted film

13) N. K. Kochetkov, *Dokl. Akad. Nauk SSSR*, **84**, 289 (1952).

14) N. K. Kochetkov, I. Ambrush, I. I. Ambrush and E. S. Severin, *Zh. Obsch. Khim.*, **28**, 3024 (1958).

Table II. Wave numbers (cm^{-1}) of the absorption bands of β-halogenovinyl ketones below 1500 cm^{-1}

Compound	Assignment								
	CH_3 asym	CH_2 scissor.	CH_3 sym	H/C=C/H in-plane	H/C=C/H out-of-plane	D/C=C/D in-plane	D/C=C/D out-of-plane	C-Cl stretch *s-trans*	C-Cl stretch *s-cis*
$CH_3COCH=CHBr$ (II)	1424m		1365 s	1291m	946 s				
$CH_3COCH=CHI$ (III) liquid	1418m		1361 s	1286m	948 s				
$CH_3COCH=CHI$ (III) crystalline	1420m		1363w	a)	958 s				
$C_2H_5COCH=CHCl$ (IV) IR spectrum	1459m	1412m	1378m	1288w	944 s			846 s	800 s
$C_2H_5COCH=CHCl$ (IV) Raman spectrum	1458m	1410m	1378vw	1290vs	b)			840m	800m
$C_2H_5COCD=CDCl$ (V)	1460m	1411m	1379m			952m	701 s	794vs	769vs
$C_2H_5COCH=CHBr$ (VI)	1460m	1411m	1379m	1283m	946 s				
$C_2H_5COCH=CHI$ (VII) liquid	1453m	1408m	1376m	1287w	948vs				
$C_2H_5COCH=CHI$ (VII) crystalline	1454m	1410m	1377m	1286w	961vs				
n-$C_3H_7COCH=CHCl$ (VIII)	1458m	1458m 1406m	1371m	1292m	943 s			853m	829m
n-$C_3H_7COCD=CDCl$ (IX)	1467m	1467m 1414m	1378m			960m	701 s	774 s	761 s
i-$C_3H_7COCH=CHCl$ (X)	1470 s		1388 s 1370m	1292m	943vs			846 s	779vs
i-$C_3H_7COCD=CDCl$ (XI)	1467 s		1387m 1370w			953m	698 s	793 s	759vs
$(CH_3)_3CCOCH=CHCl$ (XII)	1466m 1478 s		1397m 1370m	1308m	940 s				837 s

a) Absent from the spectrum of crystalline film. b) Very weak or absent from Raman spectrum.

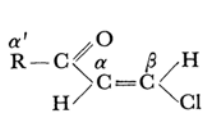
were calibrated with polystyrene and indene.[12] The frequencies are accurate to within ±1—2 cm^{-1}.

Results and Discussion

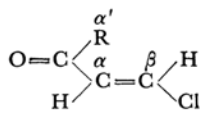
Tables I and II contain spectral data of all compounds examined; in addition representative spectra are depicted in the figures.

The spectra of the great majority of the compounds examined exihibit more peaks in the 1500—1750 cm^{-1} region than expected for molecules containing one C=O and one C=C bond; where only two peaks occur, at least additional shoulders can be observed. The occurrence of these additional absorption bands and/or shoulders cannot be explained by association effects since their intensities are practically independent of concentration. For instance, the relative intensity of the four absorption bands between 1500 and 1700 cm^{-1} in the spectrum of ethyl chlorovinyl ketone remains practically unchanged when the initial 2.4×10^{-1} M solution is diluted to 3.4×10^{-2} M concentration. Besides, the intensity of the band occurring at the lowest of these frequencies increases in hexane solution as compared with pure liquid, while exactly an opposite effect would be expected if association played any role here. *Cis-trans* isomerism can also be excluded in this discussion since β-chlorovinyl ketones were shown by NMR spectra to consist in at least 95% of the trans form[7] and the additional infrared bands are too strong to be caused by small admixtures of other molecules. Moreover substances I, IV and XII were proved by gas-liquid chromatography to be homogeneous in about 99%.

In the previous paper of this series it has been shown that methyl-β-chlorovinyl ketone[8] exists in two rotational forms. No doubt, this is also true for the β-halogenovinyl ketones studied in this work. The present results concerning spectra of several differently substituted homologues of the parent methyl-β-chlorovinyl ketones provide strong support for this concept although neither simplification of the spectra upon crystallization (compounds I, IVand V) nor any marked temperature dependence of the intensity of the absorption bands could be observed in the majority of cases (see, however, discussion on iodo ketones, III and IV, p. 2570). The two rotational forms are



s-cis



s-trans

12) R. N. Jones and A. Nadeu, *Spectrochim. Acta*, **20**, 1175 (1964).

most likely the *s-cis* and *s-trans* ones, the latter being more stabilized by resonance.

According to the data of Jones and Noack[5] and to the Stuart-Briegleb atomic models the *s-cis* form is free of strain while the *s-trans* one is sterically hindered. Therefore, the C=O group in the latter conformation is probably forced out of the plane of the C=C bond, especially in the higher homologues. However, the true gauche form is not likely to exist as its formation would mean a considerable loss of resonance energy; hence, with increasing size of the α'-substituent, the equilibrium between the *quasi-s-trans* form* and the plane, strain-free *s-cis* one will tend to shift towards the latter. This tendency is clearly illustrated by the spectra of five ketones (I, IV, VIII, X and XII) bearing different alkyls in α' position (Fig. 2). In all but one (XII) of these spectra the carbonyl band is distinctly split; the peak occurring at lower frequency (B) weakens with increasing volume of the α' substituent (in XII only an inflection is observable) thus permitting its assignment to the sterically hindered *s-trans* form; consequently band A can be attributed to the *s-cis* form. The remaining chloro ketones investigated here (II, III, V—VII, IX, XI) fit well in this scheme (see discussion below). With the olefinic C=C stretching vibrations the situation is somewhat more complex. In the majority of cases splitting of the $\nu_{C=C}$ band could not be observed; it is likely that the bands of the two conformers coincide in the spectra. The same was noted for unsubstituted α, β-unsaturated ketones.[6] *t*-Butyl-β-chlorovinyl ketone exhibits two intense bands at frequencies consistent with the $\nu_{C=C}$ vibration, but these do not seem to correspond to different conformational forms, since the lack of a distinct second $\nu_{C=O}$ band suggests rather a mono-component system. Besides, the whole spectrum is much simpler than those of the other compounds investigated. Therefore, the splitting in this particular case is probably due to other factors, possibly to Fermi resonance. Only one of the compounds investigated here: 1-chloropenten-1-one-3 (IV, Fig. 3) shows in the double-bond spectral region four intense bands (A, B, C, D), two of which (C, D) can be attributed to the $\nu_{C=C}$ vibrations in the two rotational isomers. The assignments follow from the intensity changes of these bands in solvents of various polarity: in neat liquid and in solution in acetonitrile, bands B and C increase markedly in intensity as compared with the solution in hexane; this simultaneous change means that band C is due to the $\nu_{C=C}$ vibration of the *s-trans* form, since band B was assigned in the above discussion of Fig. 2 to this form. Band D corresponds therefore to $\nu_{C=C}$ of the *s-cis* form.

The authors are aware of the dangers of interpretation based solely on intensity changes in solvents. Nevertheless, the range of these changes exceeds here so much the values expected for the pure solvent effect on band intensity that the interpretation postulating the equilibrium shift *s-cis* $\rightleftarrows$ *s-trans* seems to be justified, provided Fermi

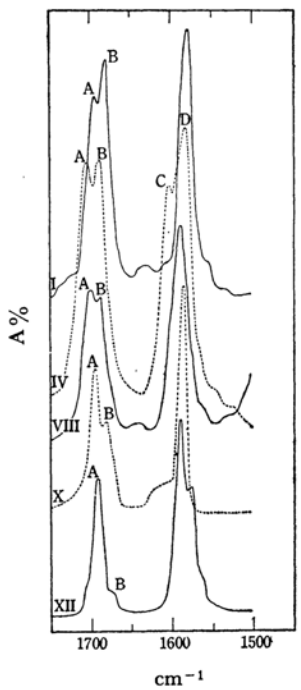


Fig. 2. Infrared spectra of β-chlorovinyl ketones in nonpolar solvents.
I: methyl-, IV: ethyl-, VIII: *n*-propyl-, X: isopropyl-, XII: *t*-butyl-β-chlorovinyl ketones.
Solvent concentrations and cell thicknesses are given in Table I.

* Called further *s-trans*.

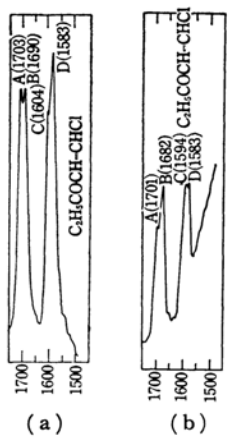


Fig. 3. Infrared spectrum of 1-chloropenten-1-one-3 (IV).
(a) C_6H_{12} solution (b) CH_3CN solution
Concentrations and cell thicknesses are given in Table I.

resonance is not involved.

The assignments derived here are in agreement with those obtained for unsubstituted α,β-unsaturated ketones.[5,6] In particular, the regularity, consisting in wider frequency separation between the C=O and C=C stretching bands in the case of the *s-cis* isomer, can now be extended on corresponding β-chloro substituted ketones. For *s-cis* 1-chloropenten-1-one-3 $\nu_{C=O}-\nu_{C=C}=120$ cm^{-1} and for *s-trans* $\Delta\nu=86\ cm^{-1}$, both values being considerably greater in comparison with those for ketones lacking polar substituents as well as with those containing the dialkylamino group in the β position, where the corresponding differences can be evaluated at about 90 cm^{-1} for the *s-cis* and 70 cm^{-1} or less for *s-trans* form. The fact, that in chloro ketones the differences $\nu_{C=O}-\nu_{C=C}$ are greater than in unsubstituted ketones, while in enamino ketones[3] they are equal or smaller, can be readily understood since a halogen is known to lower the $\nu_{C=C}$ frequency and to enhance the $\nu_{C=O}$ one, whereas an amino substituent lowers both of them, $\nu_{C=O}$ being usually somewhat more shifted.

Furthermore, the assignments presented above can be reconciled with the Raman intensities of 1-chloropenten-1-one-3 (IV, Fig. 4) on the basis of the idea of the in-phase and out-of-phase stretching vibrations of the two double bonds in the system O=C–C=C. In the Raman spectrum bands B and D are very intense while A and C occur in hexane solution as inflections only being undetectable in neat liquid. According to Sobolev and Alexanyan,[15] (see also discussion in[8]) (1) the intense Raman bands of α,β-unsaturated ketones are due to the in-phase vibration both in the *s-trans* and in the *s-cis* form, the bands due to corresponding out-of-phase vibrations being much weaker and (2) the in-phase and out-of-phase vibrations have a reverse order of frequencies in these two rotational isomers, i. e. $\nu_{sym}>\nu_{as}$ in the *s-trans* form, and $\nu_{sym}<\nu_{as}$ in the *s-cis* one. Our results fit in very well in this scheme: the intense Raman band B assigned to the $\nu_{C=O}$ vibration of the *s-trans* form has its counterpart in the weak inflection C due to the $\nu_{C=C}$ mode of the same form (i. e. $\nu_{sym}\approx\nu_{C=O}$ and $\nu_{as}\approx\nu_{C=C}$); correspondingly, inflection A and band D can be ascribed to the C=O and C=C stretch respectively in the *s-cis* form (i. e. $\nu_{as}\approx\nu_{C=O}$ and $\nu_{sym}\approx\nu_{C=C}$).

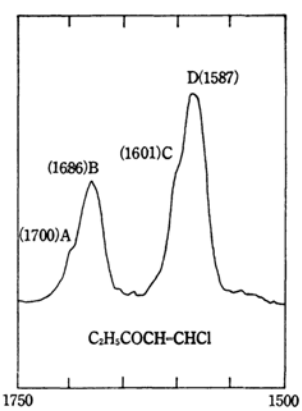


Fig. 4. Raman spectrum of 1-chloropenten-1-one-3; 50% by weight solution in hexane.

In addition to the five β-chlorovinyl ketones discussed above seven other β-halogenovinyl ketones (II, III, V—VII, IX and XI) were examined in order to investigate the influence of bromine, iodine and deuterium substituents on the position of the $\nu_{C=O}$ and $\nu_{C=C}$ bands. It is obvious that all these compounds exist likewise in two rotational forms, since (1) their liquid-state and solution spectra contain additional bands and/or shoulders in the 1700—1500 cm^{-1} region and (2) the spectra of solid methyl- and ethyl-β-iodovinyl ketones (III and VII) are markedly simplified between 650 and 1500 cm^{-1} as compared with the liquids: the bands 1286, 1237, 1150 and 864 cm^{-1} disappear from the spectrum of solid III and band 1273 cm^{-1} from that of solid VII. The fact that crystallization causes simultaneous complication in the 1700—1500 cm^{-1} region (Fig. 5), instead of the expected simplification, can be explained by assuming splittings by crystal field. In other respects the assignments of the $\nu_{C=O}$ and $\nu_{C=C}$ bands coincide with those for chloro ketones (Table I).

The solvent sensitivity of the $\nu_{C=O}$ and $\nu_{C=C}$ bands of halogenovinyl ketones differs strongly from that of aminovinyl ketones.[3] While the $\nu_{C=O}$ bands of both rotational isomers are clearly solvent-sensitive (Table I), the $\nu_{C=C}$ bands are in most cases constant within the limits of experimental error, showing that—contrary to what was observed for aminovinyl ketones—mechanical coupling between the two modes is much weaker than in amino ketones. This conclusion agrees with the calculations made by Sadlej and Sadlej[16] who showed the bond orders of the single and double bonds of the system O=C–C=C to be largely equalized in enamino ketones and but slightly changed (as compared with normal values) in halogenovinyl ketones. It should be noted that the $\nu_{C=O}$ frequencies of β-halogenovinyl ketones coincide almost exactly with those of unsubstituted vinyl ketones.[6] This indicates that the mesomeric effect of halogens counterbalances the inductive effect.

A general tendency, already noticed for enamino ketones, is the lowering of the $\nu_{C=C}$ frequency by 24—31 cm^{-1} upon vinyl deuteration (Table I).

15) E. V. Sobolev and V. T. Aleksanyan, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1965**, 1336.

16) A. Sadlej and M. Sadlej, *Bull. Acad. Polon. Sci., Sér. Sci Chim.*, **13**, 625 (1965).

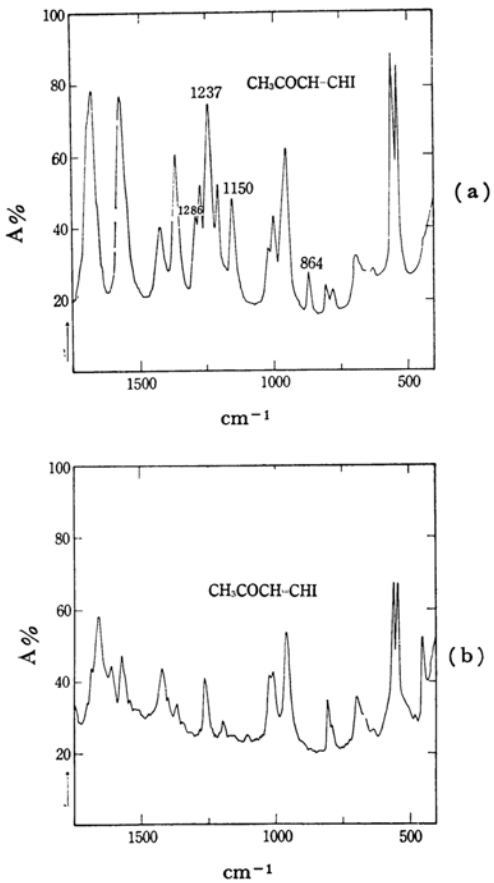


Fig. 5. Infrared spectrum of 1-iodobuten-1-one-3.
(a) liquid film, (b) crystalline film

However, the $\nu_{C=O}$ frequency is insensitive to deuteration in chloro ketones, whereas in enamino ketones the reverse is true. This demonstrates once more that mechanical coupling between $\nu_{C=C}$ and $\nu_{C=O}$ in halogenovinyl ketones is not very strong.

The spectral region below 1500 cm^{-1} cannot be fully interpreted because of the occurrence of many noncharacteristic vibrations. Yet, there are some regularities which permit to draw definite conclusions in regard to several important absorptions or, at least, to suggest tentative assignments.

First of all, the CH_2 scissoring and both the doubly degenerate and symmetrical bending modes of the CH_3 group can rather easily be recognized; the data given in Table II show that there is no marked difference with respect to aliphatic saturated ketones.[17] There are, however, in several spectra absorption bands of medium intensity between 1300 and 1358 cm^{-1}, the origin of which cannot be estimated with certainty at the time being.

The C–H vinyl bending modes were assigned on the basis of deuteration studies. The in-plane bending vibration gives rise to a band within the range 1283—1298 cm^{-1}, the only strong deviation taking place in the case of compound XII (1308 cm^{-1}). These bands shift upon deuteration to 952—960 cm^{-1}. The C–H out-of-plane vibration occurs at 940—944 cm^{-1} for chloro ketones (IV, VIII, X and XII), at 946 for bromo ketones and at 948 for iodo ketones; the band of the C–D out-of-plane vibrations of chloro ketones V, IX and XI occurs at 698—701 cm^{-1}. All isotopic shifts are of the expected magnitude ($\nu_H/\nu_D \approx 1.35$).

The assignments of the ν_{C-Cl} frequencies follow from the intensity changes in various solvents. In the previous paper[8] it was noticed, that in hexane solution the lower of the two ν_{C-Cl} bands occurring at about 800—830 cm^{-1} grows up; the same effect was now confirmed in the case of compound IV. On the basis of the interpretation of the intensity changes in the 1700—1500 cm^{-1} region (p. 2569) this frequency can be ascribed to the *s-cis* form. The ν_{C-Cl} frequency of the *s*-trans form of the non-deuteriated ketones falls in most cases to the narrow range 846—853 cm^{-1} (Raman band in IV at 840 cm^{-1}) while those of the *s-cis* form are more variable. In IV the *s-cis* ν_{C-Cl} band occurs at 800 cm^{-1} both in Raman and infrared spectra, in VIII at 829 cm^{-1}. In X first band occurs at 846 cm^{-1} and there is no other strong band in this region except that at 779 cm^{-1}. Since the band splittings in the double-bond stretching region point to rotational isomerism, the latter band can be assumed to correspond to the second conformer. For XII the situation seems to be different: the first band lies at 837 cm^{-1} and the next one at a much lower value 753 cm^{-1}; according to what was already said in the discussion on the 1700—1500 cm^{-1} region (p. 2569) it may be concluded that substance XII containing the voluminous *t*-butyl radical exists practically in one conformational form, viz. *s-cis* with a ν_{C-Cl} frequency of 837 cm^{-1}.

In vinyl deuterated compounds V, IX and XI the ν_{C-Cl} bands are displaced to lower frequencies by 20—79 cm^{-1}. Although, on the basis of the intensity data, we believe our assignments of the ν_{C-Cl} bands to be correct, we admit freely that they are not as unambiguous as was case with methyl-β-chlorovinyl ketone[8] for which no other strong bands occurred in the whole spectral region theoretically possible for the C–Cl stretching vibrations.

The ν_{C-Br} and ν_{C-I} frequencies cannot unambiguously be assigned on the basis of data now available. Assignments for other frequencies within the region 400—1500 cm^{-1} will be given in the coming paper of this series.

The spectra discussed in the present paper will be submitted to the DMS catalogue.

17) A. R. Katritzky and S. Øksne, *Spectrochim. Acta*, **17**, 1286 (1961).