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Conformations of the Esters. III. The Infrared Carbonyl Absorptions and Conformations of Propionates, Isobutyrates, and Pivalates

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In a previous paper,[1] it has been proved that alkyl acetates take only the *s-trans* conformation within their ester group, and it has been suggested that the higher homologs of the esters also have such a conformation. However, in the homologs of carboxylic acids, a conformational heterogeneity will arise if the alkyl chain is properly substituted. The conformational heterogeneity has been reported with mono and dihaloacetates,[2,3] methoxy- and phenoxyacetates,[4,5] α-methoxypropionates, and α-methoxyisobutyrates.[5] However, few authors[6,7] have reported on the conformational heterogeneity of the esters, whose α-carbon is replaced by another carbon group (alkylacetates). The purpose of this note is to present the results of a study of the infrared spectra in the carbonyl region of alkylacetates, and to relate the crabonyl-stretching frequencies with the conformations derived by rotation about the C_{CO}–C_{α} bond.

Experimental

Materials. The required esters were prepared according to the published procedures. The purities of the samples were checked by means of their physical constants, gas-chromatographic results, NMR spectra and infrared spectra.

Apparatus. The infrared spectra were recorded on a Perkin-Elmer 112G single-beam grating spectrometer (3500—3300 cm^{-1}, 1800—1700 cm^{-1}) and a Hitachi EPI-G2 grating infrared spectrophotometer (4000—400 cm^{-1}). The measurement of the spectra and the separation of the bands of esters were carried out as has been described previously.[1]

Results and Discussion

Table 1. Carbonyl absorptions of propionates, isobutyrates, and pivalates (c 0.05 mol/l)

	Compound	CS_2		CH_3CN		DMSO	
		cm^{-1}	ε	cm^{-1}	ε	cm^{-1}	ε
I	$EtCO_2Me$	1735	(148)	1731	(84)		
		1744	(702)	1739	(689)		
II	$EtCO_2Et$	1730	(127)	1723	(103)		
		1737	(841)	1733	(693)		
III	$EtCO_2$ *i*-Pr	1733	(790)	1729	(575)		
VI	$EtCO_2$ *t*-Bu	1726	(88)	1718	(76)		
		1732	(691)	1727	(562)		
V	$EtCO_2$ *t*-Am	1725	(117)	1716	(80)		
		1731	(891)	1725	(518)		
VI	*i*-$PrCO_2Me$	1733	(143)	1723	(78)		
		1740	(846)	1735	(678)		
VII	*i*-$PrCO_2Et$	1726	(101)	1721	(90)		
		1735	(902)	1730	(749)		
VIII	*i*-$PrCO_2$ *i*-Pr	1723	(183)	1715	(43)		
		1731	(870)	1724	(709)		
IX	*i*-$PrCO_2$ *t*-Bu	1729	(183)	1716	(72)		
		1730	(998)	1724	(1102)		
X	*t*-$BuCO_2Me$	1722	(138)	1722	(263)	1722	(527)
		1735	(1094)	1734	(387)	1732	(236)
XI	*t*-$BuCO_2CD_3$	1732	(501)	1726	(720)		
XII	*t*-$BuCO_2Et$	1728	(948)	1722	(894)		
XIII	*t*-$BuCO_2$ *t*-Bu	1725	(716)[a]	1713	(479)		

a) in CCl_4 c=0.0004 mol/l

As the model compounds of alkylacetates, some propionates, isobutyrates, and pivalates were chosen. These esters have been reported to have only one carbonyl absorption,[2,3,5,8,9] and no authors have reported the unsymmetric nature of the carbonyl bands of these esters. We measured the carbonyl absorption shapes carefully with a infrared spectrometer of a high resolution. The results are given in Table 1. Clearly, propionates and isobutyrates give bifurcated band in the carbonyl region except for only one case (compound III). These results may be taken as indicating the presence of two conformers if they are proved to be really carbonyl bands. The bifurcation can be attributed neither to the solute-solute interaction nor to the solute-solvent interaction, because the spectra were measured with a solution of a very low concentration and two-peaked absorptions are observed even in carbon tetrachloride. The origin of the bifurcation is also difficult to explain from the standpoint of Fermi resonance for the following two reasons. The solvent effects on the band shapes of the almost all the propionates and isobutyrates are hardly affected at all by solvent polarity. The independency of the relative intensity of the solvent polarity can be attributed to the small difference in the polarities of the conformers. On the other hand, it is well known that in the case of the Fermi resonance, the intensities of the two peaked absorptions of the carbonyl region are dramatically affected by the solvent polarity; in fact, a reversal of the intensity ratio is often observed[10] (see also the case of methyl pivalate). Methyl propionate (I) has car-

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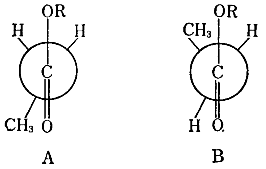
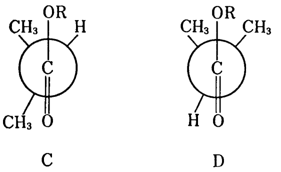
bonyl overtone absorptions of almost the same shape at 3454 cm^{-1} ($\varepsilon=0.45$) and 3472 cm^{-1} ($\varepsilon=3.56$). These two facts rule out the possibility of the bifurcation of the carbonyl bands being due to the Fermi resonance.

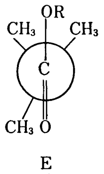
Thus, it is most likely that the bifurcation comes from the presence of at least two conformations. Three stable conformations can arise corresponding to the rotation about the C–O bond in the alcohol part. However, if this is the only cause of the bifurcation, it is difficult to explain why the methyl and *t*-butyl propionates give two absorptions in this region. This consideration leads to the conclusion that the presence of the two bands is most probably attributable to the rotational isomers about the C_{CO}–C_α bond, as is shown in Fig. 1.



Propionates



Isobutyrates



Pivalates

Fig. 1. Possible conformations of alkyl propionate, isobutyrate, and pivalate.

According to the above considerations, pivalate esters should give only one C=O band, because they have only one conformation, E, due to the symmetry of the *t*-butyl group. The results with ethyl and *t*-butyl pivalates conform to this expectation, but methyl pivalate unexpectedly gives a two-peaked band. In order to test the possibility of a Fermi resonance, the C=O absorption spectrum of methyl-d_3 pivalate (XI) was measured. It gives only one symmetrical peak. This necessarily means that the mode of C–H vibration is responsible for the bifurcation of the carbonyl band and strongly suggests that the phenomenon is caused by the Fermi resonance. Auxiliary support for this explanation has been obtained by the dramatic solvent effect on the carbonyl absorptions. Now it is clear that the bifurcation of the carbonyl bands of some simple esters reflects the heterogeneity of the conformations.

There then remains the problem of assigning the two bands to each conformation. Comparing the wave number where the carbonyl absorptions of acetates and pivalates occur, the higher frequency band may be assigned to the C–H and C=O eclipsed forms, B and D. Then it may be taken that these B and D conformers are more stable than the A and C conformers, judging from the integrated intensities of the respective bands. However, it is well known that, for unknown reasons, the C–H and C=O eclipsed conformers are less stable than the C–CH_3 and C=O eclipsed conformers. Therefore, these two contradictory arguments must be settled before establishing the assignments. We do not dare to assign the bands at present, but would like simply to point out the need of further work.

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