INFRARED SPECTRA AND CONFORMATION OF SUBSTITUTED METHYL CYCLOHEXANECARBOXYLATES AND 2-HYDROXYCYCLOHEXANECARBOXYLATES*

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Infrared bands due to carbonyl and hydroxyl stretching vibration were measured for 32 esters of substituted cyclohexane and *trans*-decalin carboxylic acids and 2-hydroxy acids. The bands were computer-separated and most of them assigned to the appropriate rotamers. The conformational equilibrium in methyl *trans*-2-hydroxy-*cis*-4-isopropylcyclohexanecarboxylate was determined using comparison of integrated intensities of the hydroxyl bands of the mobile compound with those of the conformationally biased standards. The OH/$COOCH_3$ vicinal interaction was found to be attractive (about 2·6 kJ mol^{-1}).

In the course of our stereochemical investigations (*e.g.* ref.[1-8]) we prepared many substituted cyclohexanecarboxylic, 2-methylcyclohexanecarboxylic and 2-hydroxycyclohexanecarboxylic acids and their esters. Many of them are conformationally homogeneous and thus represent valuable material for the study of defined conformational situations. We measured the infrared spectra of these compounds in the region of carbonyl stretching vibration and in the case of the 2-hydroxy esters also in the hydroxyl stretching region.

EXPERIMENTAL

All the esters, except *XXIV*, *XXV*, and *XXVI*, have been prepared previously. They were distilled before measurement and were homogeneous according to gas–liquid chromatography. The pertinent references are listed in Table I and II. The spectra were measured on a Perkin–Elmer 621 instrument in $2·5 . 10^{-3}$M solutions in tetrachloromethane at 30°C. The frequency calibration was done by polystyrene foil (band at 1601 cm^{-1}), the accuracy being $\pm 0·5$ cm^{-1}. Each compound was measured at least twice. The spectral bands were separated numerically on an Elliott 503 computer using the usual programme[9-11]. The occurrence of Fermi resonance in the carbonyl region is highly improbable since in dimethyl sulfoxide the spectra of of the studied compounds contain the same number of bands.

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TABLE I

Wavenumbers (ν, cm^{-1}), Half-Widths ($\Delta\nu 1/2$, cm^{-1}) and Apparent Integrated Intensities (B, l cm^{-2} mol^{-1}) of the Carbonyl Bands in the Esters *I*—*XV*

Compound (ref.)	ν	$\Delta\nu 1/2$	$B \,.\, 10^{-3}$	Compound (ref.)	ν	$\Delta\nu 1/2$	$B \,.\, 10^{-3}$
I[18]	1 738	8·0	13·0	*IX*[21]	1 735	6·5	14·0
II[19]	1 736	8·0	13·4	*X*[21]	1 734	7·5	12·3
III[19]	1 737	7·8	14·6	*XI*[21]	1 729·5	6·9	4·2
IV[20]	1 737	7·8	14·4		1 737	5·2	8·6
V[18]	1 734	7·5	11·3	*XII*[21]	1734	7·2	10·9
VI[19]	1 735·5	8·0	11·9	*XIII*[21,23]	1 730	7·3	3·7
VII[19]	1 736	8·0	12·5		1 736·5	5·6	8·4
VIII[20]	1 729	5·8	7·5	*XIV*[21,23]	1736	8·0	13·4
	1 735	4·9	3·8	*XV*[21]	1 736	8·1	13·3

TABLE II

Wavenumbers (ν, cm^{-1}), Half-widths ($\Delta\nu 1/2$, cm^{-1}) and Apparent Integrated Intensities (B, lcm^{-2} mol^{-1}) of the Carbonyl and Hydroxyl Bands in the Hydroxy Esters *XVI*—*XXXII*

Compound (ref.)	Carbonyl bands			Hydroxyl bands		
	ν	$\Delta\nu 1/2$	$B \,.\, 10^{-3}$	ν	$\Delta\nu 1/2$	$B \,.\, 10^{-3}$
			trans-Hydroxy esters			
XVI[1]	1 724	10·0	10·5	3 542	59·4	3·0
	1 737	6·1	1·6	3 597	22·7	2·4
	1 743	5·6	1·5	3 622	8·2	0·4
XVII[2]	1 723	9·7	9·6	3 545	51·6	2·6
	1 735	7·7	2·4	3 597	22·7	2·2
	1 742	6·3	1·9	3 622	9·3	0·5
XVIII[8]	1 725	10·1	10·9	3 538	58·9	3·1
	1 738	6·2	1·4	3 591	22·4	2·0
	1 744	5·5	1·7	3 616	10·6	0·5
XIX[4]	1 725	11·1	12·1	3 545	51·6	2·6
	1 737	5·6	1·2	3 597	23·5	2·5
	1 743	5·2	1·3	3 622	9·7	0·5
XX[8]	1 723	10·5	10·2	3 547	44·4	2·0
	1 734	7·7	2·4	3 596	21·3	2·0
	1 742	5·6	1·6	3 621	10·2	0·6

TABLE II
(*Continued*)

Compound (ref.)	Carbonyl bands			Hydroxyl bands		
	ν	Δν1/2	$B . 10^{-3}$	ν	Δν1/2	$B . 10^{-3}$
XXI[5]	1 724	12·1	10·1	3 539	29·4	1·6
	1 738	6·4	1·3	3 598	22·9	2·2
	1 744	6·4	1·4	3 622	9·9	0·5
XXII[8]	1 724	9·9	10·3	3 541	58·0	3·1
	1 736	7·0	1·8	3 599	28·4	3·2
	1 743	5·3	1·4	3 624	8·8	0·3
XXIII[a,26]	1 723	11·2	9·9	3 543	53·6	2·5
	1 734	8·7	2·0	3 597	22·1	2·0
	1 742	6·3	2·1	3 622	9·9	0·5
XXIV[b]	1 736	8·1	12·8	3 625	9·2	2·4
XXV[c]	1 736	8·5	13·7	3 625	8·7	2·2
XXVI[c,7]	1 724	10·9	7·3	3 544	56·7	1·9
	1 735	7·3	5·4	3 596	22·3	1·4
	1 742	6·0	2·1	3 623	8·6	1·2
			cis-Hydroxy esters			
XXVII[1]	1 721	7·5	10·9	3 545	40·0	6·7
	1 728	4·8	0·5	3 610	26·0	0·5
	1 743	8·2	2·5	3 624	10·4	0·3
XXVIII[5]	1 718	5·5	6·0	3 538 w	43·5	6·9
	1 722	6·4	4·0	3 593	52·6	1·0
	1 743	7·8	2·6	3 628	16·4	0·6
XXIX[8]	1 719·5	7·0	10·4	3 546	39·5	7·2
	1 741·5	8·7	2·5	3 622	22·2	0·8
XXX[a,26]	1 720	6·8	10·5	3 547	38·5	5·7
	1 742	10·2	3·5	3 605	33·3	0·9
XXXI[1]	1 716	7·4	9·5	3 548	39·3	6·6
	1 738	9·6	2·5	3 596	6·7	0·1
XXXII[5]	1 719	7·0	8·4	3 545	43·5	6·3
	1 741	9·7	2·9	3 619	27·1	0·7

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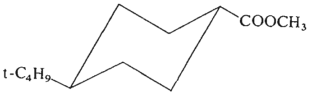
[a] Already studied (ref.[15,24,25]). [b] B.p. 141°C/10 Torr; for $C_{12}H_{22}O_3$ (214·3) calculated: 67·25% C, 10·35% H; found: 67·06% C, 10·29% H. [c] B.p. 140°C/10 Torr; elemental analysis: calculated as for *XXIV*; found: 67·30% C, 10·17% H. [d] B.p. 135°C/10 Torr; for $C_{11}H_{20}O_3$ (200·3) calculated: 65·97% C, 10·07% H; found: 65·96% C, 10·15% H.

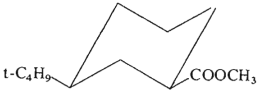
RESULTS AND DISCUSSION

Esters without Hydroxyl

The spectral data for this series of esters (Scheme 1) are given in Table I. As seen from the values found for the esters *I – VII*, the wavenumbers of the carbonyl bands of axial ester groups are only very slightly lower than those of the equatorial ones (1 734 to 1 736 cm^{-1} and 1 736 – 1 738 cm^{-1}, respectively). Some of the bands are perfectly symmetrical, some of them exhibit a negligible asymmetry at the low-frequency side which we attribute to the presence of minor amounts of other rotamers of the ester group[12]. A vicinal methyl, not interacting with the ester group, has no effect on the carbonyl stretching vibration, as illustrated by the spectra of the axial esters *V* and *X* (ν(C=O) 1 734 cm^{-1} for both compounds).

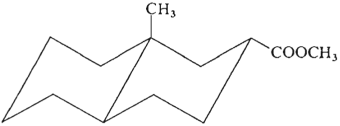


I

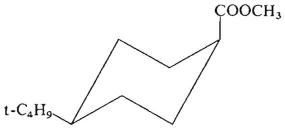


II

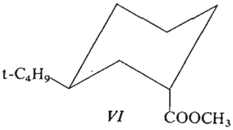
III



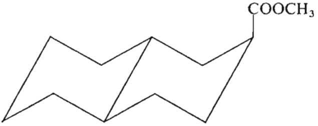
IV



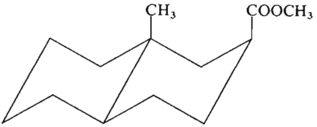
V



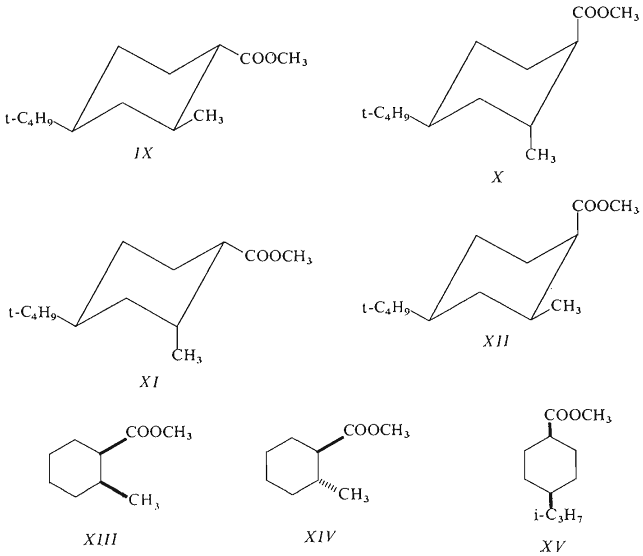
VI



VII



VIII

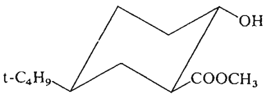


SCHEME 1

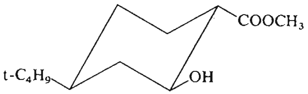
The ester *XI*, in which the methyl group is axial and the ester function equatorial, exhibits a medium band at 1737 cm^{-1} and another, weaker one, at 1729 cm^{-1}. We believe that the band splitting is of conformational origin and that the low-wavenumber band is due to a conformer in which there is an interaction between the two groups. The same situation is found in the case of the compound *VIII* in which the methyl group is in the syn-axial position relative to the ester group. Whereas the equatorial 9-methyl derivative *IV* exhibits a $\nu(C{=}O)$ band at the same wavenumber as the nor-derivative *III* (1737 cm^{-1}), its epimer *VIII* with the axial ester group shows two bands (at 1729 and 1735 cm^{-1}), differing thus significantly from its nor-analogue *VII* which displays only one band at 1736 cm^{-1}. Also here the same explanation can be offered, namely that in the ester *VIII* the band at 1729 cm^{-1} may be due to a rotamer with an interaction between the methyl and the ester group. This behaviour resembles the splitting of the hydroxyl band in the spectrum of 2β-hydroxy-9β-methyl-*trans*-decalin, analogous to the ester *VIII* (hydroxyl instead of the ester group)[11].

Hydroxy Esters

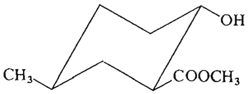
The spectral data for the hydroxy esters *XVI–XXXII* (Scheme 2) are given in Table II. As expected, the diaxial compounds *XXIV* and *XXV* exhibit only free hydroxyl bands at 3625 cm^{-1} and one carbonyl band at 1736 cm^{-1}, showing thus that – similarly to methyl – the hydroxy group has only a negligible polar effect on the ester carbonyl stretching vibration (*cf.* the band at 1734 cm^{-1} and 1735·5 cm^{-1} for *V* and *VI*, respectively).



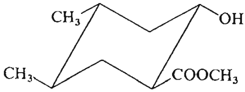
XVI



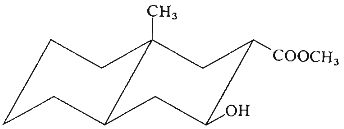
XVII



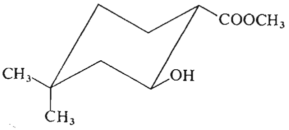
XVIII



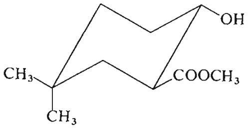
XIX



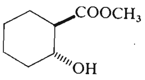
XX



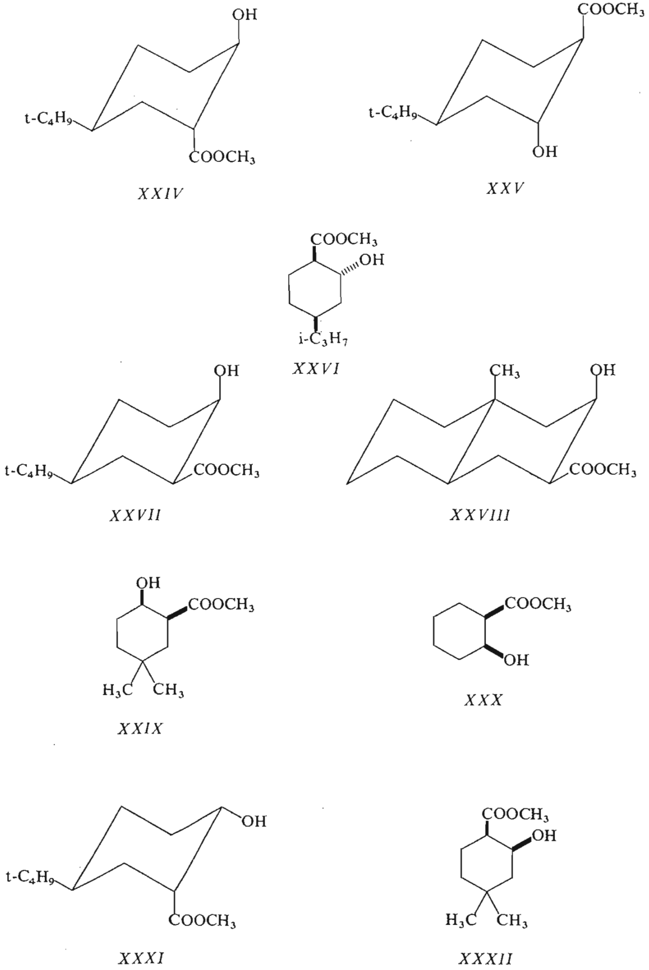
XXI



XXII



XXIII


OH
t-C_4H_9
$COOCH_3$
XXIV
$COOCH_3$
t-C_4H_9
OH
XXV
$COOCH_3$
OH
i-C_3H_7
XXVI
OH
t-C_4H_9
$COOCH_3$
XXVII
CH_3
OH
$COOCH_3$
XXVIII
OH
$COOCH_3$
H_3C
CH_3
XXIX
$COOCH_3$
OH
XXX
OH
t-C_4H_9
$COOCH_3$
XXXI
$COOCH_3$
OH
H_3C
CH_3
XXXII

SCHEME 2

In the hydroxyl region, esters with equatorial hydroxyl and ester groups have spectra of a very characteristic shape (Fig. 1). We have used this shape many times as a proof of a diequatorial conformation of a 2-hydroxy ester[8]. The spectra display three types of OH-bands: one free at about 3620 cm^{-1} and two bonded at about 3595 cm^{-1} and at about 3540 cm^{-1}. According to the previous studies[13-17], these bands should correspond to non-bonded species (type A), the O—H···O—C=O hydrogen bond (type B) and the O—H···O=C—O hydrogen bond (type C), respectively. From the comparison with the integrated intensities of the free hydroxyl band in the "diaxial" compounds *XXIV* and *XXV* the amount of free hydroxyl in the diequatorial esters *XVI*–*XXIII* can be estimated to be about 20%. Unfortunately, we are not able to draw further conclusions concerning the exact population of these three species since we do not know the "intrinsic" molar integrated intensities of the bands due to single conformers.

In the spectra of the hydroxy esters we see at the first glance two C=O bands at 1723–1725 cm^{-1} and at 1739–1742 cm^{-1}, the ratio of their integrated intensities being for the diequatorial esters invariably 4 : 1. However, since in the hydroxyl region we observe three distinct types of hydroxyl we should expect also three carbonyl bands, corresponding to the types A, B, and C. We therefore adjusted the separation programme so as to obtain three bands although separation into only two bands gave an equally good fit. We are aware of formality of this procedure and we take the parameters of thus-obtained bands as only informative. Since the carbonyl band belonging to type C is known to be shifted to lower wavenumbers whereas that due to the type B is displaced to higher values[13-17], the strong low-wavenumber band at about 1724 cm^{-1} corresponds to the type C of hydrogen bond. The smaller bands at about 1734 cm^{-1} and about 1743 cm^{-1} should be due to the types A and Bs respectively. As seen from Table II, the percentages of the free hydroxyl bands (a,

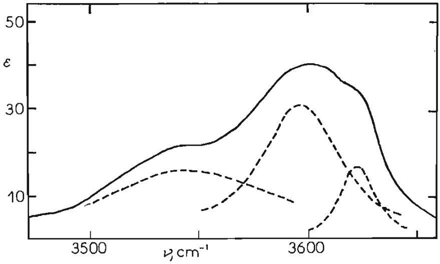


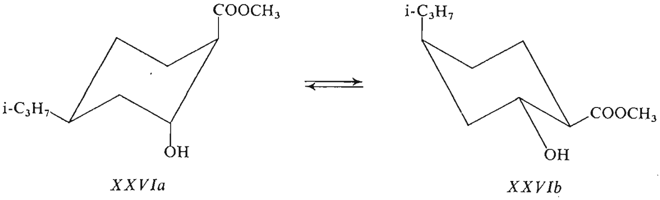
FIG. 1

Typical Spectrum of a "Diequatorial" Hydroxy Ester (compound *XVII* in CCl_4)

calculated *e.g.* from the data for *XXIV* or *XXV*) do not correspond very well to those of the free C=O bands (type A) thus obtained (calculated *e.g.* also from *XXIV* and *XXV*); this shows that the method in this case gives only qualitative information about the population of the single rotamers in the hydroxy esters studied.

Conformational Equilibrium in XXVI *and* $OH/COOCH_3$ *Diequatorial Vicinal Interaction*

The spectrum of *XXVI* shows signs of conformational non-homogeneity. Using the diequatorial (*XVII*) and diaxial (*XXV*) standards it should be possible to estimate the corresponding conformational population of the diaxial (*XXVIa*) and diequatorial (*XXVIb*) forms (Scheme 3). We compared three bands: two bonded hydroxyl bands, corresponding to the diequatorial conformer *XXVIb* (at 3544 and 3596 cm^1) and one free hydroxyl band (at 3623 cm^{-1}). The population of the diequatorial conformer *XXVIb*, as calculated from the respective band intensities, is 66%, 61% and 60%.



SCHEME 3

We take thus the value 62% as reliable. This means that the conformer *XXVIb* is by about 1·3 kJ mol^{-1} more stable than the other one (*XXVIa*). If we take the conformational preference for the $COOCH_3$ group as 5·0 kJ mol^{-1}, for hydroxyl 2·5 kJ . . mol^{-1} and for isopropyl 8·8 kJ mol^{-1} (ref.[22]), then the vicinal interaction between equatorial hydroxyl and equatorial methoxycarbonyl groups, $OH/COOCH_3$, is attractive and amounts to about 2·6 kJ mol^{-1}. This value is comparable with that of the vicinal $OH/N(CH_3)_2$ interaction found previously[4] using the same approach but it differs from the value of $OH/COOCH_3$ estimated in methanol[7] (about 0·0 kJ . mol^{-1}), in which evidently the weak intramolecular hydrogen bond between the hydroxyl and ester groups is superseded by intermolecular hydrogen bonding with the solvent.

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