

# INFRARED SPECTRA OF 4,6-DIDEOXYHEXONIC LACTONES IN THE REGIONS OF STRETCHING VIBRATIONS OF THE CARBONYL AND HYDROXY GROUPS\*

K. KEFURT<sup>a</sup>, P. ADÁMEK<sup>b\*\*</sup> and J. JARÝ<sup>a</sup>

<sup>a</sup> Laboratory of Monosaccharides and

<sup>b</sup> Department of Inorganic Chemistry,

Prague Institute of Chemical Technology, 166 28 Prague 6

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Infrared absorption bands of the  $\nu(\text{C}=\text{O})$  ( $1800-1700\text{ cm}^{-1}$ ) and  $\nu(\text{OH})$  ( $3700-3400\text{ cm}^{-1}$ ) vibrations of four diastereoisomeric lactones of 4,6-dideoxyhexonic acids of the configurations *L-ribo*, *L-xylo*, *L-arabino*, and *L-lyxo*, their di-O-methyl derivatives, 2-O-benzoyl derivatives, lactones of 2-O-methyl-4,6-dideoxy-D-*xylo*-hexonic acid, of 3-O-methyl-4,6-dideoxy-D-*xylo*-hexonic acid, and of (*S*)-(-)-5-hydroxycaproic acid were studied in dilute solutions. The band positions are discussed in terms of the structure and steric conditions of the molecules and compared with the results of <sup>1</sup>H-NMR and CD measurements.

In our previous work<sup>1</sup> we have studied the conformation of lactones of 4,6-dideoxyhexonic acids. <sup>1</sup>H-NMR and CD spectra favour the half-chair conformation for the diastereoisomers of the *ribo* and *xylo* configurations and the boat conformation for those of the *arabino* and *lyxo* configurations. In relation to that study we measured now infrared spectra of the lactones in question in the regions of stretching vibrations of the carbonyl ( $\nu(\text{C}=\text{O})$ ) and hydroxy ( $\nu(\text{OH})$ ) bonds. Useful information on the conformation of sugar compounds can be obtained from measurements of dilute solutions in nonpolar solvents, where the intramolecular, but not the intermolecular hydrogen bonds occur. The formation, intensity, and population of those bonds is conditioned by the steric structure of the molecule<sup>2</sup>. The position of the absorption band of the  $\nu(\text{C}=\text{O})$  vibrations is being used to support an assignment of the conformation to the six-membered lactone ring, too; this is based on the results of the work of Cheung, Overton and Sim<sup>3</sup>, who attributed the  $\nu(\text{C}=\text{O})$  range of  $1750-1730\text{ cm}^{-1}$  to lactones in the half-chair form and the range of  $1765$  to  $1758\text{ cm}^{-1}$  to those in the boat form. These conclusions resulted from the study of a rather small set of substances, all of non-sugar nature. In sugar lactones, formation of intramolecular hydrogen bonds to the carbonyl group can bring about

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\*\* Present address: State Research Institute of Material, 113 12 Prague 1.

a shift of the  $\nu(\text{C}=\text{O})$  absorption band to lower wavenumbers<sup>4,5</sup> and so a false conclusion concerning the lactone conformation, if it was made based on the rule<sup>3</sup> mentioned. The data obtained with the set of substances measured in the present work make it possible to assess the effect of intramolecular hydrogen bonds and other factors on the position of the band followed and so to test the applicability of the rule<sup>3</sup> to sugar lactones. The conclusions obtained from the analysis of the spectra in the regions of stretching vibrations of the hydroxy and carbonyl groups are in this work related to the results of <sup>1</sup>H-NMR and CD measurements.

## EXPERIMENTAL

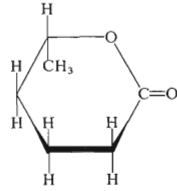
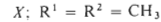
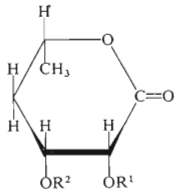
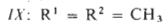
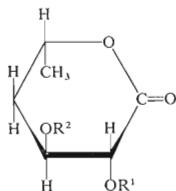
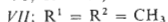
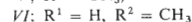
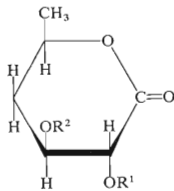
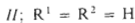
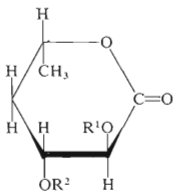
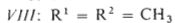
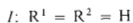
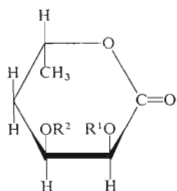
*Substances measured:* Lactone of 4,6-dideoxy-L-ribo-hexonic acid<sup>6</sup> (I), lactone of 4,6-dideoxy-L-xylo-hexonic acid<sup>7</sup> (II), lactone of 4,6-dideoxy-L-arabino-hexonic acid<sup>8</sup> (III), lactone of 4,6-dideoxy-L-lyxo-hexonic acid<sup>9</sup> (IV), lactone of 4,6-dideoxy-2-O-methyl-D-xylo-hexonic acid<sup>10</sup> (V), lactone of 4,6-dideoxy-3-O-methyl-D-xylo-hexonic acid<sup>10</sup> (VI), lactone of 4,6-dideoxy-2,3-di-O-methyl-D-xylo-hexonic acid<sup>10</sup> (VII), lactone of 4,6-dideoxy-2,3-di-O-methyl-L-ribo-hexonic acid<sup>10</sup> (VIII), lactone of 4,6-dideoxy-2,3-di-O-methyl-L-arabino-hexonic acid<sup>10</sup> (IX), lactone of 4,6-dideoxy-2,3-di-O-methyl-L-lyxo-hexonic acid<sup>10</sup> (X), lactone of 2-O-benzoyl-4,6-dideoxy-L-ribo-hexonic acid<sup>10</sup> (XI), lactone of 2-O-benzoyl-4,6-dideoxy-L-xylo-hexonic acid<sup>10</sup> (XII), lactone of 2-O-benzoyl-4,6-dideoxy-L-arabino-hexonic acid<sup>10</sup> (XIII), lactone of 2-O-benzoyl-4,6-dideoxy-L-lyxo-hexonic acid<sup>10</sup> (XIV), and lactone of (S)-(–)-5-hydroxycaproic acid<sup>11</sup> (XV).

*Infrared spectra* of the substances were measured in tetrachloromethane solutions ( $5 \cdot 10^{-4}$  to  $1.5 \cdot 10^{-3}$  M) on a grating spectrometer Perkin-Elmer 325 at room temperature. Quartz cells, 20 mm thick, were used for measurements in the  $\nu(\text{OH})$  region, and KBr cells, 6 mm thick, for measurements in the  $\nu(\text{C}=\text{O})$  region.

## RESULTS AND DISCUSSION

The positions of the absorption peaks of the compounds investigated are given in Table I. Considering the position of the  $\nu(\text{C}=\text{O})$  band of the nonsubstituted lactones I–IV in terms of the above-mentioned rule<sup>3</sup>, we find an agreement with the rule in that the absorption peaks of the “half-chair”<sup>1</sup> lactones of the *ribo* (I) and *xylo* (II) configurations lie in the range of  $1750\text{--}1730\text{ cm}^{-1}$  and those of the “boat”<sup>1</sup> lactones of the *arabino* (III) and *lyxo* (IV) configurations are shifted to higher wavenumbers. As mentioned above, however, the  $\nu(\text{C}=\text{O})$  band position can be affected in sugar lactones by the formation of an intramolecular hydrogen bridge with the neighbouring hydroxy group<sup>4,5</sup>. This effect really appears, as is obvious from the comparison of the  $\nu(\text{C}=\text{O})$  wavenumber of the 2-O-methyl derivative V with that of the 3-O-methyl derivative VI: in the latter case, where the formation of the intramolecular hydrogen bridge  $\text{C}_{(2)}\text{—O—H}\cdots\text{O}=\text{C}_{(1)}$  is possible, the  $\nu(\text{C}=\text{O})$  band has a virtually the same position as that of the nonsubstituted lactone II, whereas in the former case, where the formation of this bridge is eliminated by the substitution in the position 2, the band of the nonbonded carbonyl group is shifted to  $1757\text{ cm}^{-1}$ . A similar shift to

higher wavenumbers ( $1775-1753\text{ cm}^{-1}$ ) can be found in the spectra of all the di-O-methyl derivatives VII–X, and it is somewhat more pronounced in the case of the 2-O-benzoyl derivatives XI–XIV  $1783-1763\text{ cm}^{-1}$ . Consequently, the  $\nu(\text{C}=\text{O})$  wavenumbers of lactones with substituted OH group at  $\text{C}_{(2)}$ , i.e. of the compounds V and VII–XIV, lie beyond the ranges determined by Cheung and coworkers for lactones in the half-chair or in the boat conformation, and attain considerably higher values than as reported usually for six-membered lactones<sup>12-14</sup>.



These findings cannot be explained as accounted for by a possible change in the conformation of the substances discussed, as the values of the interaction constants in the  $^1\text{H-NMR}$  spectra virtually do not vary on the substitution at the lactone ring<sup>1</sup>. For an explanation we proceed from the idea that the position of the  $\nu(\text{C}=\text{O})$  band in the spectra of six-membered lactones can be affected by two factors acting in opposite directions. One of them, tending to increase the  $\nu(\text{C}=\text{O})$  wavenumber, is the strain brought about by the interaction of the  $\text{C}=\text{O}$  group with the equatorial substituent at  $\text{C}_{(2)}$ . (The term "equatorial" is used here to denote a substituent bonded

by an pseudoequatorial or bowsprit bond to the  $C_{(2)}$  atom of the lactone ring in the half-chair or the boat conformation). From molecular models this interaction can be seen to be different for the boat and the half-chair conformations. In lactones possessing the boat conformation the carbonyl oxygen and the equatorial substituent at  $C_{(2)}$  are lined up in the eclipsed arrangement (Fig. 1A), whereas in the half-chair conformation the carbonyl group, as observed from the  $C_{(1)}-C_{(2)}$  bond direction, lies approximately between the two bonds radiating from the  $C_{(2)}$  carbon (Fig. 1B). Obviously the interaction increases with the bulk of the substituent at  $C_{(2)}$ , to a higher extent for lactones in the boat conformation than for those in the half-chair conformation. In this manner we are able to explain the high-frequency shift of the  $\nu(C=O)$  band of lactones occurring predominantly in the boat conformation as compared with the diastereoisomers existing predominantly in the half-chair conformation, as well as the higher wavenumbers of this band in the spectra of the 2-O-benzoyl derivatives XI–XIV in comparison with the 2-O-methyl derivative V or the di-O-methyl derivatives VII–X. To support this idea we can point to the  $\nu(C=O)$  wavenumbers found in the spectra of the lactone XV (Table I) or of *cis*- and *trans*-3,5-dimethylvalerolactones<sup>15,16</sup> as well as a series of steroid lactones<sup>17</sup> in the range of 1744–1736  $\text{cm}^{-1}$ , hence in the range reported for the  $\nu(C=O)$  absorption of six-membered lactones<sup>12–14</sup>; in all these cases only hydrogen substituents are attached to the second carbon atom of the lactone chain. In accordance with the above idea one could expect slightly higher wavenumbers of the  $\nu(C=O)$  vibrations also for the lactones I–IV due to steric interaction of the C=O and OH groups. In these compounds, however, the second factor, *viz.* the intramolecular hydrogen bond  $C_{(2)}-O-H\cdots O=C_{(1)}$ , occurs, acting in the opposite direction; it makes the  $\nu(C=O)$  wavenumber return to the range usual for lactones with hydrogen substituents at  $C_{(2)}$  only.

We can thus conclude that the validity of the Cheung–Overton–Sim rule<sup>3</sup> has been verified with our series of lactones in that lactones occurring predominantly in the boat conformation exhibit absorption of the carbonyl stretching at higher wavenum-

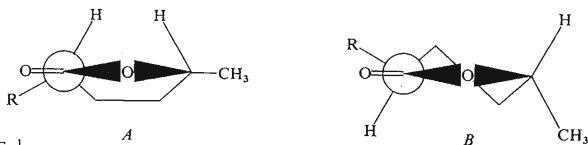


FIG. 1

Projections of the Boat (A) and Half-Chair (B) Conformations of the Lactones Studied in the Direction of the  $C_{(1)}-C_{(2)}$  Bond

bers than their diastereoisomers occurring predominantly in the half-chair conformation. On the other hand, however, the  $\nu(\text{C}=\text{O})$  bands in the spectra of most of the substances measured lie beyond the limits given<sup>3</sup> for the two conformations of a six-membered lactone ring; using the rule mentioned one has to take into account the possibility that the position of the  $\nu(\text{C}=\text{O})$  band can be affected not only by the steric structure of the lactone ring, but also by the detail structure in the very vicinity of the carbonyl group, particularly by the bulk and nature of the equatorial substituent at  $\text{C}_{(2)}$ .

In the region of  $3700\text{--}3400\text{ cm}^{-1}$ , two bands corresponding to the stretching vibrations of bonded OH groups were found in the spectra of the nonsubstituted lactones *I*–*IV* (Table I); one of them lies in the range of  $3550\text{--}3502\text{ cm}^{-1}$ , the other in the range of  $3601\text{--}3576\text{ cm}^{-1}$ . For an assignment of these bands to particular hydroxy groups we proceeded from two assumptions: 1. The occurrence of the band of an OH group in one of the two ranges is governed by the type of its intramolecular

TABLE I

Positions ( $\text{cm}^{-1}$ ) of the Bands of Stretching Vibrations of the Carbonyl and Hydroxy Groups in the Infrared Spectra of Diastereoisomeric Lactones of 4,6-Dideoxyhexonic Acids and Their Derivatives

Measured at room temperature in 0.0015–0.0005M solutions in tetrachloromethane. Characteristics of the bands: s strong, m medium, w weak, br broad.

| Substance   | $\nu(\text{C}=\text{O})$<br>(lactone) | $\nu(\text{C}=\text{O})$<br>(ester) | $\nu(\text{H}-\text{O})-\text{C}_{(3)}$ | $\nu(\text{H}-\text{O})-\text{C}_{(2)}$ | Conformation <sup>a</sup> |   |                  |
|-------------|---------------------------------------|-------------------------------------|---|---|---------------------------|---|------------------|
| <i>I</i>    | 1 743 s                               | —                                   | 3 583 s                                 | 3 532 s                                 | H                         |   |                  |
| <i>II</i>   | 1 745 s                               | —                                   | 3 601 s                                 | 3 550 m                                 | H                         |   |                  |
| <i>III</i>  | 1 753 s                               | —                                   | 3 599 s                                 | 3 520 m                                 | B                         |   |                  |
| <i>IV</i>   | 1 757 s                               | —                                   | 3 576 s                                 | 3 502 s                                 | B                         |   |                  |
| <i>V</i>    | 1 757 s                               | —                                   | 3 597 s                                 | —                                       | H                         |   |                  |
| <i>VI</i>   | 1 742 s                               | —                                   | —                                       | 3 540 s                                 | H                         |   |                  |
| <i>VII</i>  | 1 753 s                               | —                                   | —                                       | —                                       | H                         |   |                  |
| <i>VIII</i> | 1 753 s                               | —                                   | —                                       | —                                       | H                         |   |                  |
| <i>IX</i>   | 1 767 s                               | —                                   | —                                       | —                                       | B                         |   |                  |
| <i>X</i>    | 1 775 s                               | —                                   | —                                       | —                                       | B                         |   |                  |
| <i>XI</i>   | 1 768 s                               | 1 739 s                             | 1 725 w                                 | 3 613 s                                 | 3 520 w,br                | — | H                |
| <i>XII</i>  | 1 763 s                               | 1 742 s                             | 1 725 w                                 | 3 613 s                                 | 3 505 w,br                | — | H                |
|             |                                       |                                     | 1 711 w                                 |   |                           |   |                  |
| <i>XIII</i> | 1 772 s                               | 1 741 s                             | 1 710 s                                 | 3 605 s                                 | 3 505 s,br                | — | B                |
| <i>XIV</i>  | 1 783 s                               | 1 737 s                             | 1 710 w                                 | 3 610 s                                 | 3 530 w,br                | — | B                |
| <i>XV</i>   | 1 744 s                               | —                                   | —                                       | —                                       | —                         | — | H-B <sup>b</sup> |

<sup>a</sup> H half-chair, B boat, from <sup>1</sup>H-NMR and CD spectra; <sup>b</sup> ref.<sup>15</sup>.

hydrogen bond ( $\text{O}-\text{H}\cdots\text{O}-\text{H}$  or  $\text{O}-\text{H}\cdots\text{O}=\text{C}$ ). 2. The position of the band within the corresponding range depends on the steric conditions of formation of the pertinent hydrogen bridge. In fact, here the well-known fact is considered that the strength of an intramolecular hydrogen bond is reflected by the magnitude of the shift of the band of the bonded OH group from the position of that of a free OH group to lower wavenumbers<sup>2</sup>. In accordance with the assumption (1) we attribute the bands of the lactones *I-IV* in the range of  $3550-3502\text{ cm}^{-1}$  to the stretching of the hydroxy group at  $\text{C}_{(2)}$  bonded *via* an intramolecular hydrogen bridge to the oxygen of the neighbouring carbonyl group (shifts  $\Delta\nu(\text{OH})$   $80-128\text{ cm}^{-1}$ )\*. This assignment is supported by the comparison of the  $\nu(\text{OH})$  wavenumbers in the spectra of the 3-O-methyl derivative *VI* ( $3540\text{ cm}^{-1}$ ,  $\Delta\nu(\text{OH}) = 90\text{ cm}^{-1}$ ) and the 2-O-methyl derivative *V* ( $3597\text{ cm}^{-1}$ ,  $\Delta\nu(\text{OH}) = 33\text{ cm}^{-1}$ ). Of these two monomethyl derivatives only the compound *VI* can form an intramolecular hydrogen bond to the carbonyl group. The band position of the 2-O-methyl derivative *V* also supports the assignment of the bands of the lactones *I-IV* in the region of  $3601-3576\text{ cm}^{-1}$  to the stretching of the OH groups at  $\text{C}_{(3)}$  hydrogen-bonded to the oxygen atom at  $\text{C}_{(2)}$  ( $\Delta\nu = 54$  to  $30\text{ cm}^{-1}$ ).

Finer differences in the positions of the  $\nu(\text{OH})$  absorption bands in the spectra of diastereoisomeric compounds can result from different steric conditions of intramolecular hydrogen bond formation, particularly different distances of the two bonded oxygen atoms and geometries of the bridges formed. Investigating these factors on models of the lactones *I-IV* built up according to the data of their <sup>1</sup>H-NMR spectra, we find more favourable steric conditions for the formation of the intramolecular  $\text{C}_{(2)}-\text{O}-\text{H}\cdots\text{O}=\text{C}_{(1)}$  hydrogen bond in lactones occurring in the boat conformation (*III* and *IV*) than in those occurring in the half-chair conformation (*I* and *II*). As these conditions are equal within each pair of the compounds, we might expect the  $\nu(\text{OH})$  wavenumbers for the OH group at  $\text{C}_{(2)}$  in the spectra of the lactones *III* and *IV* equal or very close to each other, and analogously for the pair *I* and *II*. The results given in Table I, however, do not agree with this expectation. This disagreement can be explained in terms of the influence of the hydroxy group at  $\text{C}_{(3)}$ . The absence of the band of the free hydroxy group from the spectra of the lactones *I-IV* indicates that the hydroxy group at  $\text{C}_{(2)}$  takes part in the formation of the hydrogen bond to the carbonyl group and simultaneously, through its oxygen atom, in the formation of the  $\text{C}_{(3)}-\text{O}-\text{H}\cdots\text{O}-\text{C}_{(2)}$  bridge. As has been shown<sup>18-21</sup>,

\* Since no absorption band of stretching vibrations of a free secondary hydroxy group has been found in the spectra of any of the compounds measured, we compare the wavenumbers with the value of  $3630\text{ cm}^{-1}$ , reported for such a band<sup>12</sup>. The  $\Delta\nu(\text{OH})$  values are then of significance only for a comparison of strengths of intramolecular hydrogen bonds of the same type in compounds of related nature, which is satisfied in this work.

the vibrational frequency of a hydroxy group engaged in this manner simultaneously in two hydrogen bridges is lower, with the decrease obviously depending on the strength of the intramolecular hydrogen bond to the central oxygen atom of this double bridge. In each of the mentioned pairs of diastereoisomeric lactones with the same conformation, one isomer has more favourable steric conditions for the formation of the intramolecular  $C_{(3)}-O-H\cdots O-C_{(2)}$  bond, as in its molecule the OH group at  $C_{(3)}$  can fall into a plane containing the directed orbital of one of the lone electron pairs of the oxygen atom at  $C_{(2)}$ . In the pair of the "boat lactones" the isomer of the *lyxo* configuration (*IV*) is so favoured, in the other pair this is the lactone of the configuration *ribo* (*I*). In the remaining two lactones, *II* and *III*, this situation does not take place: in their molecules the OH bond at  $C_{(3)}$  cannot lie in a plane, which would simultaneously contain either of the orbitals of the lone electron pairs of the oxygen atom at  $C_{(2)}$  (the spatial orientation of the orbitals at that atom is always fixed owing to the intramolecular bond  $C_{(2)}-O-H\cdots O=C_{(1)}$ ). The effect of the intramolecular hydrogen bond on the decrease of the wavenumber of the  $\nu(\text{OH})$  absorption band of the hydroxy group at the second carbon atom is therefore more pronounced in lactones of the configuration *ribo* (*I*) and *lyxo* (*IV*) than in the diastereoisomers of the configuration *xylo* (*II*) and *arabino* (*III*). We find therefore the absorption band of the stretching vibrations of the OH group at  $C_{(2)}$  in the spectra of the lactones *I* and *IV* lying at lower wavenumbers than those in the spectra of the lactones *II* and *III*, respectively.

The results obtained can be thus interpreted as follows: 1. The strongest bridges  $C_{(2)}-O-H\cdots O=C_{(1)}$  ( $3502\text{ cm}^{-1}$ ,  $\Delta\nu = 128\text{ cm}^{-1}$ ) and  $C_{(3)}-O-H\cdots O-C_{(2)}$  ( $3576\text{ cm}^{-1}$ ,  $\Delta\nu = 54\text{ cm}^{-1}$ ) found from the spectral data of the lactone in the *lyxo* configuration, *IV*, are enabled by the favourable steric conditions for the formation of both the former bridge (boat conformation) and the latter bridge (favourable mutual arrangement of the hydroxy groups at  $C_{(2)}$  and  $C_{(3)}$ ). The  $\nu(\text{OH})$  wavenumber of the hydroxy group at the second carbon atom is in addition lowered due to the occurrence of the double hydrogen bridge. 2. The weakest bridges  $C_{(2)}-O-H\cdots O=C_{(1)}$  ( $3550\text{ cm}^{-1}$ ,  $\Delta\nu = 80\text{ cm}^{-1}$ ) and  $C_{(3)}-O-H\cdots O-C_{(2)}$  ( $3601\text{ cm}^{-1}$ ,  $\Delta\nu = 29\text{ cm}^{-1}$ ) were found in the lactone of the *xylo* configuration, *II*, which in the half-chair conformation lacks any of the favourable conditions, as described above, for the formation of strong bridges. 3. The lactone of the *arabino* configuration, *III*, forms, owing to the favourable conditions in the boat conformation, a rather strong bridge to the carbonyl group ( $3520\text{ cm}^{-1}$ ,  $\Delta\nu = 110\text{ cm}^{-1}$ ), which, however, is not affected by the weaker bridge  $C_{(3)}-O-H\cdots O-C_{(2)}$  ( $3599\text{ cm}^{-1}$ ,  $\Delta\nu = 31\text{ cm}^{-1}$ ) to such an extent as was the case with the isomer *IV*. 4. The lactone of the *ribo* configuration, *I*, possesses in the half-chair conformation an orientation of the hydroxy groups at  $C_{(2)}$  and  $C_{(3)}$  favourable for the formation of a relatively strong  $C_{(3)}-O-H\cdots O-C_{(2)}$  bridge ( $3583\text{ cm}^{-1}$ ,  $\Delta\nu = 47\text{ cm}^{-1}$ ) which affects *via*

the double bridge the  $\nu(\text{OH})$  wavenumber of the hydroxy group at  $\text{C}_{(2)}$ , so that its value ( $3532 \text{ cm}^{-1}$ ,  $\Delta\nu = 98 \text{ cm}^{-1}$ ) is lower than that for the isomer *II*.

So the  $\nu(\text{OH})$  band positions in the spectra of the lactones *I–IV* can be reasonably interpreted assuming the substances to occur in the conformations as inferred from the  $^1\text{H-NMR}$  and CD spectral measurements.

In the spectra of the 2-O-benzoyl derivatives *XI–XIV*, a strong absorption band is found in the range of  $3613–3605 \text{ cm}^{-1}$ . In the spectrum of the lactone *XIII*, an additional, approximately equally pronounced but broader band appears at  $3505 \text{ cm}^{-1}$ . In the spectra of the lactones *XI*, *XII*, and *XIV*, broad, not very marked peaks can be found in the range of  $3530–3505 \text{ cm}^{-1}$ , too. The band of a free hydroxy group was not observed in the spectra of the compounds examined. For an assignment of those bands we proceed from the theoretical possibility of intramolecular hydrogen bond formation from the OH group at  $\text{C}_{(3)}$  either to the alkoxy or to the carbonyl oxygen of the ester group at  $\text{C}_{(2)}$ . The band between  $3613$  to  $3605 \text{ cm}^{-1}$  belongs obviously to the hydroxy group bonded by a weak bridge to the alkoxy oxygen (five-membered ring). The lower strength of this bridge as compared with the analogous type of bridge in the nonsubstituted lactones *I–IV* can be explained by the effect of the neighbouring benzoyl group, which brings about drain of electrons from the alkoxy oxygen to the carbonyl carbon. We attribute the absorption at lower wavenumbers ( $3530–3505 \text{ cm}^{-1}$ ) to the  $\nu(\text{OH})$  vibrations of the hydroxy group bonded by an intramolecular hydrogen bond to the carbonyl oxygen of the benzoyl group (seven-membered ring). This assignment is also consistent with the position of the  $\nu(\text{C}=\text{O})$  band. The bands in the spectra of the lactones *XI–XIV* observed in the range of  $1783–1762 \text{ cm}^{-1}$  belong obviously to the lactone carbonyl, as they follow by their position the above-discussed relation of  $\nu_{\text{max}}$  to the conformation. In the range of  $1742–1737 \text{ cm}^{-1}$ , pronounced bands appear in the spectra of all the lactones discussed; they correspond probably to the  $\nu(\text{C}=\text{O})$  vibrations of the ester group, where the alkoxy oxygen is bonded by a hydrogen bridge to the neighbouring hydroxy group (five-membered ring). In the spectrum of the lactone *XIII*, an equally intense additional band appears at  $1710 \text{ cm}^{-1}$ , in the spectrum of the lactone *XII* two minor bands lie at  $1725$  and  $1711 \text{ cm}^{-1}$ . These bands, as well as the unresolved band at  $1725 \text{ cm}^{-1}$  in the spectrum of the lactone *XI* and the indistinct band at  $1710 \text{ cm}^{-1}$  of the lactone *XIV* are to be ascribed to the  $\text{C}=\text{O}$  bond of the benzoyl group hydrogen-bonded to the hydroxy group at  $\text{C}_{(3)}$  (seven-membered ring). Our present information on the internal hydrogen bond does not confirm a direct relation between the energy of that bond and its population, the latter being affected by some additional factors. Based on the comparison of steric conditions of formation of seven- and five-membered bridges, performed with models of the substances under study, a favoured presence of the former bridge in the lactones *XII* and *XIII* and that of the latter bridge in the lactones *XI* and *XIV* could be



expected, if the benzoyl group is assumed to occur in the planar trans arrangement. The observed absorptivities of the bands treated, however, indicate rather the formation of a five-membered bridge to the alkoxy oxygen of the ester group to prevail in all the benzoyl derivatives discussed except for the lactone *XIII*.

## REFERENCES

1. Kefurt K., Snatzke G., Snatzke F., Trška P., Jarý J.: *This Journal* 41, 3324 (1976).
2. Tichý M.: *Advan. Org. Chem.* 5, 115 (1965).
3. Cheung K. K., Overton K. H., Sim G. A.: *Chem. Commun.* 1965, 634.
4. Henbest H. B., Lovell B. J.: *J. Chem. Soc.* 1957, 1965.
5. Bruice T. C., Fife T. H.: *J. Amer. Chem. Soc.* 84, 1973 (1962).
6. Lukeš R., Jarý J., Němec J.: *This Journal* 27, 735 (1962).
7. Jarý J., Kefurt K.: *This Journal* 31, 2059 (1966).
8. Němec J., Kefurtová Z., Kefurt K., Jarý J.: *This Journal* 33, 2097 (1968).
9. Kefurt K., Kefurtová Z., Jarý J.: *This Journal* 36, 1701 (1971).
10. Kefurt K., Kefurtová Z., Jarý J.: *This Journal*, 41, 1791 (1976).
11. Kuhn R., Jerchel D.: *Ber. Deut. Chem. Ges.* 76, 413 (1943).
12. Nakanishi K.: *Infrared Absorption Spectroscopy, Practical*. Holden-Day, San Francisco 1964.
13. Colthup N. B., Daly L. H., Wiberley S. E.: *Introduction to Infrared and Raman Spectroscopy*. Academic Press, New York—London 1964.
14. *IRSCOT—Infrared Structural Correlation Tables* (R. G. J. Miller, H. A. Willis, Eds). Heyden, London 1965.
15. Korver O.: *Tetrahedron* 26, 2391 (1970).
16. Carrol F. I., Blackwell J. T.: *Tetrahedron Lett.* 1970, 4173.
17. Sheppard R. C., Turner S.: *Chem. Commun.* 1968, 77.
18. Bellamy L. J., Pace R. J.: *Spectrochim. Acta* 22, 525 (1966).
19. Staněk J. jr, Adámek P., Čapek K., Jarý J.: *Carbohyd. Res.*, in press.
20. Kefurt K., Staněk J. jr, Kefurtová Z., Jarý J.: *This Journal* 40, 300 (1975).
21. Marek M., Kefurt K., Staněk J. jr, Jarý J.: *This Journal* 41, 2596 (1976).

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