ISOMERIC OXATRICYCLODECANONES WITH NON-PLANAR LACTONE GROUPS: SYNTHESIS, ABSOLUTE CONFIGURATION, NMR AND X-RAY STUDY

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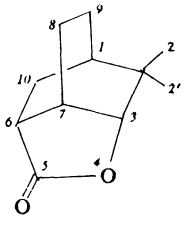
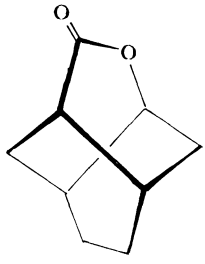
Several rigid polycyclic lactones, potentially suitable as models for investigation of the lactone grouping geometry, were synthesized. (3*S*)-4-Oxatricyclo[4.3.1.0^{3,7}]decan-5-one ((+)-*I*), (3*R*)-5-oxatricyclo[4.3.1.0^{3,8}]decan-4-one ((+)-*III*) and (4*S*)-5-oxatricyclo[5.2.1.0^{4,8}]decan-6-one ((−)-*VIII*) were prepared by acid-catalyzed lactonization of (2*R*)-*endo*-bicyclo[2.2.2]oct-5-ene-2-carboxylic acid. (1*S*)-4-Oxatricyclo[4.4.0.0^{3,8}]decan-5-one ((−)-*II*) was synthesized from (2*S*,5*S*)-*endo*,*endo*-bicyclo[2.2.2]-octane-2,5-dicarboxylic acid. The structure of *VIII* was unequivocally proved by its NMR spectra and the geometry of *III* was determined by X-ray analysis. The absolute configuration of (+)-*III* was assigned by correlation with (1*R*)-bicyclo[3.2.1]nonan-6-one. The acid-induced interconversion of *I*, *II*, *III* and *VIII* was studied. Lactones *II* and *III* represent suitable rigid models for investigations of non-planar lactone groups of known chirality and geometry.

Studies of spatial arrangement of the amide group, motivated by the importance of the amide (peptide) bond in protein structures, were given a new impulse by the finding that in the crystalline state peptide groups often have non-planar arrangement[1] and that such arrangements may be present even in solutions[2]. Using model lactams we have shown[3-7] that the differences between planar (local symmetry C_s) and non-planar (local symmetry C_1) amide groupings can be reflected sensitively particularly by chiroptical properties. Because of the known similarity of lactams and lactones one could expect an analogous behaviour of both these systems. Since lactones have received as yet much less attention[8], we decided to prepare and investigate some model lactones with non-planar functional group. Although several lactones having a non-planar —CO—O—C— grouping in the crystalline state have been described[9-14], most of these compounds are not suitable for our chiroptical investigations. They either contain other chromophores whose Cotton effects complicate analysis of the CD curves, or have interacting bonds placed in the vicinity of the lactone chromophore which change chiroptical properties of the lactone grouping, or are not rigid enough to

guarantee even an approximate similarity of the molecular geometry in crystal with that in solution. On the basis of our experience with lactams we tried to select suitable models from rigid polycyclic lactones, closely similar to the already studied lactams[3-7,15]. In our present set of models, the lactone *I* represents a planar arrangement of the functional group in a five-membered ring, whereas the heterotwistane lactone *II* contains a non-planar lactone group in a six-membered ring; the same situation exists also in the case of the lactone *III*, isosteric with protoadamantane. In this paper we describe synthesis of the mentioned lactones in their optically active forms, their interconversion, assignment of absolute configuration and also the X-ray structure determination of the lactone *III*.



I



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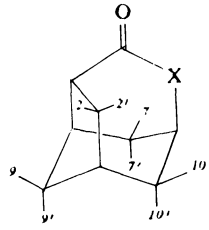


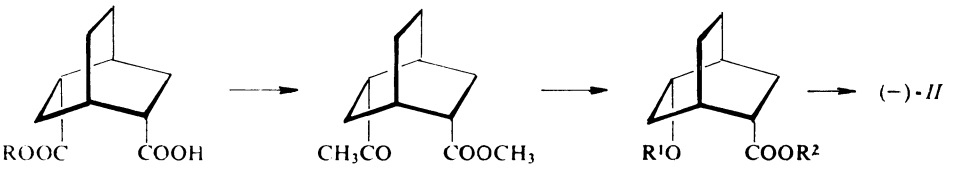
III, X = O
XII, X = NH

Synthesis and Isomerization of the Lactones

Although the racemic lactone *II* was prepared many years ago[16], its optically active form has not been described. We prepared the laevorotatory enantiomer (−)-*II** starting from (2*S*,5*S*)-*endo*,*endo*-bicyclo[2.2.2]octane-2,5-dicarboxylic acid (*IVa*) of known absolute configuration[17]. Its monomethyl ester *IVb* was converted into the keto ester *V* which on Baeyer–Villiger oxidation and saponification gave the hydroxy acid(+)-*VIb*. Its cyclization afforded the desired lactone (−)-*II* whose absolute configuration (1*S*) follows from that of the starting diacid *IVa* (Scheme 1).

The racemic lactones *I* and *III* have been prepared by lactonization of *endo*-bicyclo-[2.2.2]oct-5-ene-2-carboxylic acid (*VII*) by Moriarty and coworkers[18]. This reaction affords in principle three lactones, *I*, *III* and *VIII* (Scheme 2), whose ratio depends on the reaction time: short reaction times give the former two lactones whereas prolonged treatment with acid leads to the lactones *III* and *VIII*. The kinetics of formation shows that the kinetically preferred lactone *I* is then equilibrated into *III* and *VIII*. We have studied the equilibration of these three lactones at 25°C in 96% H_2SO_4,

* Optically active compounds are described by their sign of rotation in front of their number; for the racemates the (±) sign is not given.

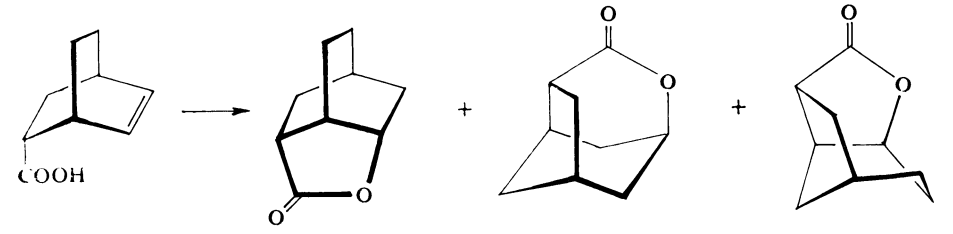


(+)-*IVa*, R = H
IVb, R = CH_3

V

VIa, $R^1 = CH_3CO$, $R^2 = CH_3$
VIb, $R^1 = R^2 = H$

SCHEME 1



(+)-*VII* (+)-*I* (+)-*III* (−)-*VIII*

SCHEME 2

determining the product composition by gas–liquid chromatography. The observed curves, depicted in Fig. 1, show that compounds *III* and *VIII* are practically of the same stability whereas the energy of the lactone *I* is by about 9kJ mol^{-1} higher. The interconversion $I \rightleftharpoons III$ is faster than $I \rightleftharpoons VIII$ and $VIII \rightleftharpoons III$. For comparison, we equilibrated also the twistane-like lactone *II* (ref.[16]). Already after 1 min the mixture did not contain any detectable amount of the starting compound and consisted only of the three lactones *I*, *III* and *VIII* which were equilibrated to give a mixture identical with those obtained from the other three lactones studied.

The lactones *I*, *III* and *VIII* can be separated by column chromatography on silica gel and thus the acid-catalyzed lactonization of the acid *VII* represents a method of choice for preparation of lactones *III* and *VIII*. Whereas the structure of the lactones *I* and *III* has been determined unequivocally, structure of the lactone *VIII* was suggested by Moriarty and coworkers[18] on the basis of a much weaker evidence.

We performed therefore a complete ^{13}C and ^1H NMR analysis of this compound (for data see Table I). The ^{13}C NMR spectrum exhibited signals of 9 carbon atoms. From the signal multiplicities (determined from off-resonance decoupled spectra) and chemical shifts it was possible to determine the presence of one carbonyl, one CH—O three methine and four methylene carbon atoms. The 360 MHz ^1H NMR spectrum

of *VIII* (Fig. 2) is perfectly resolved so that the multiplets of all the 12 hydrogen atoms can be identified. Using the coupling constants we can follow the topology of the whole molecule, assign positions to all the hydrogens and thus prove unequivocally the structure *VIII*.

For comparison, we tried to obtain an equally detailed ^1H and ^{13}C NMR analysis of the isomeric lactone *III* (Table II). As expected, the ^{13}C NMR spectrum showed the same number and types of the carbon atoms as in the lactone *VIII*, the chemical shifts being different. However, the 360 MHz ^1H NMR spectrum was substantially less resolved and therefore no complete interpretation could be made in deuteriochloroform or hexadeuteriobenzene even in the presence of a shift reagent.

Assignment of Absolute Configuration

Lactonization of the optically active acid (+)-*VII* which is known[17] to have the 2*R* configuration, gave the optically active lactones (+)-*I*, (+)-*III* and (−)-*VIII*. On prolonged standing in 96% sulfuric acid at 25°C the lactones only very slowly racemized (the percentage of the retained optical activity, measured by CD spectra

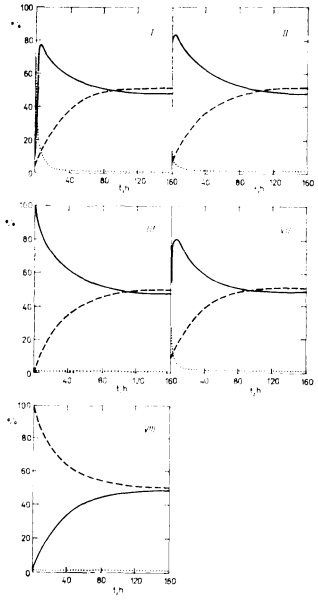


FIG. 1

Isomerization of lactones *I*, *II*, *III* and *VIII* and lactonisation of acid *VII* in 96% H_2SO_4 at 25°C; *I* ·····, *III* ———, *VIII* – – – –

for (+)-*III* was 65% after 120 h). The isomerisation was much faster than the racemization.

Whereas the formation of the lactone (+)-*I* is stereochemically straightforward, the absolute configuration at $C_{(6)}$ being the same as at $C_{(2)}$ in the acid (+)-*VII*, the lactones (+)-*III* and (−)-*VIII* arise by a complex series of rearrangements. Although a plausible rearrangement scheme has been suggested[18], it has not been proved reliably and other reaction routes cannot be excluded. Therefore the conversion of (+)-*VII* into the latter two lactones has no correlative value and other ways for configurational assignment had to be looked for. Such suitable correlation was the conversion of the lactone *III* into bicyclo[3.2.1]octan-6-one (*XI*), described[18] already for the racemic compound. We carried out this reaction sequence (Scheme 3) with (+)-*III* and obtained the leavorotatory ketone (−)-*XI* which is known[19] to have the 1*R* configuration. The lactone (+)-*III* has thus configuration, corresponding to the depicted formula. This result in turn shows that the configuration at the carboxyl-bearing atom in the starting acid (+)-*VII* was retained during the rearrangements and constitutes a further support for the suggested rearrangement mechanism[18].

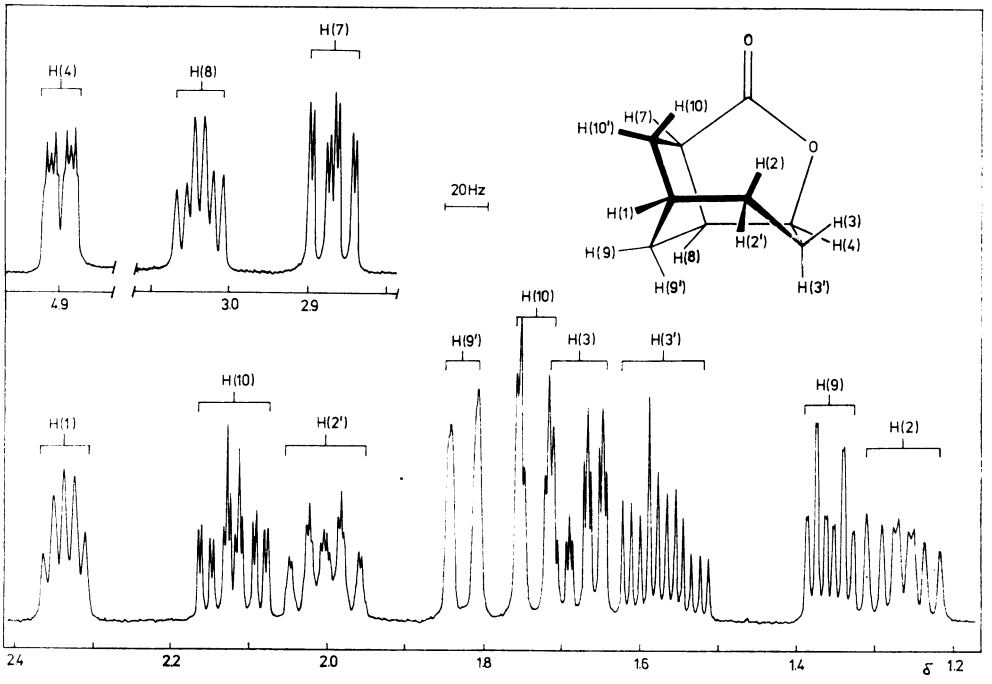


FIG. 2

^{1}H NMR Spectrum of lactone *VIII* at 360 MHz

TABLE I

^{1}H and ^{13}C NMR parameters of lactone *VIII* in deuteriochloroform

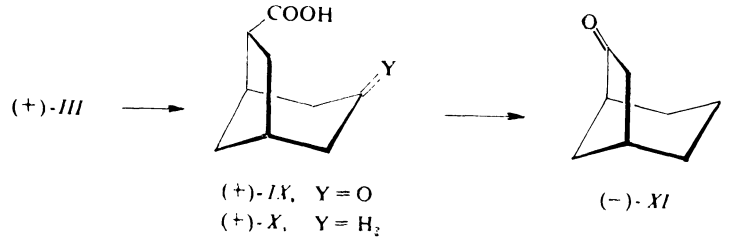
^{1}H NMR							^{13}C NMR	
Atom	δ_H	^2J	^3J			^4J, ^5J	Atom	δ_C
H(4)	4·90	—	$J_{4,3} = 1·8$	$J_{4,3'} = 3·9$	$J_{4,8} = 9·0$	$J_{4,10} = 1·1$	C(6)	181·3 s
H(8)	3·04	—	$J_{8,4} = 9·0$	$J_{8,7} = 8·0$	$J_{8,9} = 4·5$	$J_{8,1} = 0·8$	C(4)	81·2 d
			$J_{8,9'} = 0·8$				C(1)	41·8 d
H(7)	2·87	—	$J_{7,8} = 8·0$	$J_{7,10} = 1·8$	$J_{7,10'} = 11·7$	$J_{7,9'} = 0·5$	C(7)	39·9 d
H(1)	2·34	—	$J_{1,2} < 1$	$J_{1,2'} = 9·5$	$J_{1,9} = 4·4$	$J_{1,8} = 0·8$	C(8)	31·6 d
			$J_{1,9'} \sim 2$	$J_{1,10} \sim 0$	$J_{1,10'} = 5·5$		C(2)	40·9 t
H(10′)	2·12	$J_{10',10} = 13·3$	$J_{10',1} = 5·5$	$J_{10',7} = 11·7$		$J_{10',2'} = 1·6$	C(3)	30·4 t
H(2′)	2·00	$J_{2',2} = 14·7$	$J_{2',1} = 9·5$	$J_{2',3'} = 8·1$	$J_{2',3} = 1·3$	$J_{2',4} = 1·1$	C(9)	24·9 t
						$J_{2',10'} = 1·6$	C(10)	23·2 t
H(9′)	1·83	$J_{9',9} = 12·5$	$J_{9',1} = 2$	$J_{9',8} = 0·8$		$J_{9',10} = 2$		
						$J_{9',7} = 0·5$		
H(10)	1·73	$J_{10,10'} = 13·3$	$J_{10,1} \sim 0$	$J_{10,7} = 1·8$		$J_{10,9'} = 2$		
H(3)	1·68	$J_{3,3'} = 15·3$	$J_{3,2} = 6·9$	$J_{3,2'} = 1·3$	$J_{3,4} = 1·8$	—		
H(3′)	1·57	$J_{3',3} = 15·3$	$J_{3',2} = 12·1$	$J_{3',2'} = 8·1$	$J_{3',4} = 3·9$	—		
H(9)	1·36	$J_{9,9'} = 12·5$	$J_{9,1} = 4·4$	$J_{9,8} = 4·5$		—		
H(2)	1·26	$J_{2,2'} = 14·7$	$J_{2,1} < 1$	$J_{2,3} = 6·9$	$J_{2,3'} = 12·1$	—		

TABLE II

^1H and ^{13}C NMR parameters of lactone *III*

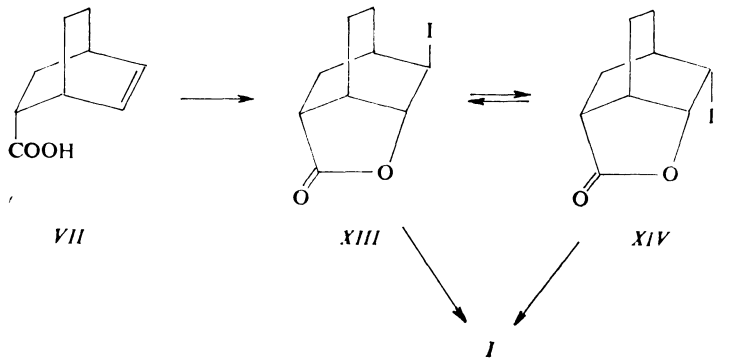
^1H NMR				^{13}C NMR	
Atom	δ_H (in $CDCl_3$)	$J_{H,H}$	δ_H (in $C_6{}^2H_6$)	Atom	δ_C (in C^2HCl_3)
H(6)	4·58	$J_{6,7} \sim J_{6,10} \sim 4{\cdot}1$ $J_{6,7'} \sim J_{6,10'} \sim 2{\cdot}5$	3·96	C(4)	177·1 s
H(3)	3·04	$J_{3,8} = 7{\cdot}6$ $J_{3,2} = 9{\cdot}8$ $J_{3,2'} = 1{\cdot}2$	2·77	C(6)	76·1 d
H(8)	2·67	$J_{8,3} = 7{\cdot}6$ $J_{8,7'} \sim J_{8,9'} \sim 6$ $J_{8,9} \sim 1$	1·90	C(1)	33·3 d
H(1)	2·44	$J_{1,9} \sim J_{1,9'} \sim J_{1,10} \sim J_{1,10'} \sim 3{\cdot}5$	1·71	C(3)	35·8 d
H(2)	2·06	$J_{2,2'} = 12{\cdot}9$ $J_{2,3} = 9{\cdot}8$ $J_{2,1} = 4{\cdot}4$ $J_{2,10} = 2$	1·67	C(8)	43·5 d
Other protons	1·69—2·00		0·93—1·49	C(2)	35·1 t
				C(7)	36·8 t
				C(9)	38·9 t
				C(10)	40·8 t

On the other hand, the very slow racemization of the lactones *I*, *III* and *VIII* indicates that also some other pathways may in part be involved in the rearrangement. Since the lactone *VIII* can arise directly from the isomer *III* by mere 1,2-hydride shift, it is very probable that the absolute configuration at the carbonyl-bearing carbon in both compounds is the same (7*R* for the lactone (−)-*VIII*).



SCHEME 3

The optical purity of the lactone (+)-*III* follows from its conversion into the lactam *XII* whose purity was proved by the ^{1}H NMR spectrum in the presence of a chiral shift reagent[20]. The five-membered lactone (+)-*I* was synthesized independently[25] *via* the iodo lactone *XIII* (Scheme 4). This reaction sequence gave lactone (+)-*I* with the same ellipticity value as had the lactone prepared by the acid-catalyzed lactonization.



SCHEME 4

The reduction of the iodo lactone *XIII* over Adams catalyst in the presence of triethylamine[22] deserves comment. When the reaction was interrupted after consumption of about half of the theoretical amount of hydrogen, three compounds were isolated by chromatography: the starting iodo lactone *XIII*, the lactone *I* and an un-

known iodine-containing compound *XIV* (Scheme 4). According to its IR spectrum (ν(CO) = 1 780 cm^{-1} in $CHCl_3$) the compound contained a five-membered lactone ring and its mass spectrum and elemental analysis showed a composition identical with that of the iodo lactone *XIII*. Its complete hydrogenation gave the pure lactone *I*. When the hydrogenation of either *XIII* or *XIV* was interrupted after more than half of the theoretical ammount of hydrogen had been consumed, identical mixtures of *XIII*, *I* and *XIV* were obtained in both cases. Evidently, the two compounds were equilibrated very rapidly (in several minutes) under the hydrogenation conditions used. However, practically no equilibration took place on stirring with prereduced platinum in the absence of either hydrogen or triethylamine. Also stirring with triethylammonium iodide alone did not bring about the isomerization.

On the basis of these observations we propose that the isomeric iodo compound is the configurational isomer *XIV* with *cis*-relationship of the iodine atom and the lactone ether oxygen.

The structure of both the iodo lactones *XIII* and *XIV* was confirmed also by their ^{13}C and ^{1}H NMR spectra and comparison with those of the lactone *I* (Table III). In the ^{13}C NMR spectra the introduction of iodine results in the expected change, *i.e.* replacement of one methylene carbon by a methine one. However, the small effect of the iodine atom on the α-carbon atom does not allow its unequivocal identification in the spectrum. Also the 200 MHz ^{1}H NMR spectra of the iodo lactones *XIII* and *XIV* are only partially interpretable. Only three protons of the lactone ring, together with the CH—I proton, are outside the envelope of the remaining protons. Since in the spectrum of *XIV* in deuteriochloroform even the CH—O and CH—I signals mutually overlap, all the three compounds were measured in hexadeuterioacetone which gave a better resolution. The suggested structures of the iodolactones *XIII* and *XIV* agree with the observed coupling constants of the H(2) and H(3) protons. For the iodo lactone *XIII* the value $J_{2,3} \leqq 1$ Hz corresponds to a torsion angle of about 90° whereas the value of $J_{2,3}$ (6·5 Hz), found for *XIV*, is compatible with the torsion angle 30° shown by Dreiding models. The coupling constant $J_{3,7}$ remains approximately constant (5 Hz) for all the three lactones *I*, *XIII* and *XIV*.

Three-Dimensional Structure Determination of the Lactone III

The X-ray analysis of lactone *III* confirms the expected marked non-planarity of the lactone grouping, the torsion angle $C_{(7)}—O_{(1)}—C_{(6)}—C_{(3)}$ being 17·14° and $C_{(7)}—O_{(1)}—C_{(6)}—O_{(2)}$ 165·10°. (For numbering of atoms in the X-ray study see Fig. 3). Both values are very similar to those found for other lactones with non-planar lactone grouping (ref.[13]). The non-planarity around the carbonyl carbon atom is characterized by the parameter χ_C which is 3·04°, the deviation of $C_{(6)}$ from the plane, determined by the other three atoms ($C_{(3)}$, $O_{(2)}$, $O_{(1)}$), amounts only to 0·0021 nm. Comparing the bond lengths and bond angles in the lactone grouping of *III* with

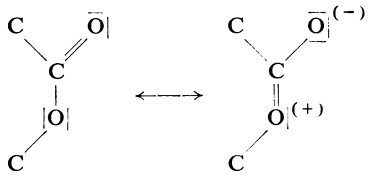
TABLE III

^{1}H and ^{13}C NMR parameters of lactones *I*, *XIII* and *XIV* in hexadeuterioacetone

^{1}H NMR				^{13}C NMR			
Atom	*I*	*XIII*	*XIV*	Atom	*I*	*XIII*	*XIV*
H(2)	1·47—1·97 m	4·45 um	4·67 bd	C(5)	180·4 s	178·9 s	178·9 s
			$J_{2,3} = 6·5$	C(3)	78·0 d	85·5 d	78·0 d
H(3)	4·63 bt	4·92 bd	4·49 bt	C(2)	33·3 t	31·0 d[a]	32·3 d[a]
	$J_{3,2} = 5·8$	$J_{3,2'} \leqq 1$	$J_{3,2} = 6·5$	C(1)	23·8 d	32·4 d	35·2 d
	$J_{3,2'} \leqq 1$	$J_{3,7} = 4·8$	$J_{3,7} = 5·0$	C(6)	34·4 d	34·6 d	36·1 d
	$J_{3,7} = 4·8$			C(7)	37·4 d	35·5 d	36·3 d
H(6), H(7)	2·38—2·51 m	2·48 m	2·53 m	C(8)	27·6 t	27·8 t	27·0 t
			2·43 m	C(9)	26·0 t	23·8 t	23·8 t
Other protons	1·47—1·97 m	1·53—2·22 m	1·53—2·09 m	C(10)	15·6 t	14·8 t	15·0 t

[a] Tentative assignment, signal can be interchanged with C(1), C(6) or C(7).

those published for other non-planar lactones we can find some differences, *e.g.* smaller ring bond angles, a longer endo C—O bond and a very short exo C—O bond (Table IV), which are probably connected with the strained polycyclic skeleton of the lactone *III*. Generally, the observed values agree with the idea that non-planarity of the lactone grouping should disfavour the dipolar structure *B* in the resonance hybride, lengthening simultaneously the endo C—O bond and shortening the exo C—H bond. Similar situation has been observed for lactams with non-planar amide groups[6,7].

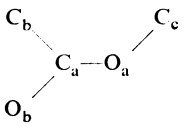


A *B*

The results, obtained with the lactone *III*, show that it can serve as a good model for a non-planar lactone group of known chirality and geometry. The same, of course, can be said about the lactone *II*. The chiroptical studies of both these models and their comparison with those of the corresponding lactams will be published in a separate paper.

TABLE IV

Comparison of geometric parameters of the lactone group in *III* and in *XV* (ref.[13])



Parameter	$C_a—O_a$[a]	$C_a—O_b$[a]	$\sphericalangle C_b—C_a—O_a$	$\sphericalangle C_a—O_a—C_c$	$\sphericalangle C_b—C_a—O_b$
III	0·1335	0·1197	116°	117°	125°
XV[b]	0·128	0·121	123°	120°	114°

[a] Bond lengths in nm; [b] 6α-bromo-17β-hydroxy-17α-methyl-4-oxa-5α-androstan-3-one.

EXPERIMENTAL

The IR spectra were measured on a Perkin–Elmer 621 instrument, CD spectra on a Jouan CD 185/II Dichrographe. The 360 MHz ^{1}H NMR spectra of compounds *III* and *VIII* were taken on a Bruker WH-360 spectrometer, the 200 MHz spectra of lactones *I*, *XIII* and *XIV* on a spectro-

meter Varian *XL*-200 in the pulse FT mode in solutions of several mg of the compounds in 0·4 ml of deuteriochloroform, hexadeuteriobenzene or hexadeuteriacetone in a 5 mm cell. The assignments were made on the basis of decoupling experiments and the chemical shifts and coupling constants were obtained by a first order analysis. The 50·3 MHz ^{13}C NMR spectra of the lactones *III* and *VIII* were taken on a Bruker WP-200 spectrometer, those of compounds *I*, *XIII* and *XIV* on a Varian XL-200 instrument. All measurements were performed with about 20 mg of the compounds in 2 ml of deuteriochloroform or hexadeuterioacetone in a 10 mm cell. The chemical shifts were obtained from ^{1}H-noise decoupled spectra (in C^2HCl_3 referenced to tetramethylsilane and in $C^2H_3COC^2H_3$ to the solvent methyl group and calculated according to the relationship $\delta_{C^2H_3} = 29{\cdot}2$) and signal multiplicities were obtained from the ^{1}H off-resonance decoupled spectra.

Gas–liquid chromatography of the lactones was performed on a Chrom 4 chromatograph (Laboratorní přístroje, Czechoslovakia; a 3·7 m column packed with 10% poly(diethylene glycol succinate), on Chromosorb W at 180°C).

X-Ray Analysis of Lactone *III*

Crystals of the lactone *III* have an orthorhombic symmetry. Refinement using a manual diffractometer DRON-1 afforded the following parameters of the unit cell: $a = 1{\cdot}1761 \pm 0{\cdot}0008$ nm, $b = 1{\cdot}0060 \pm 0{\cdot}0001$ nm, $c = 0{\cdot}6382 \pm 0{\cdot}0001$ nm. The cell contains 4 molecules. A set of 1141 independent reflections was obtained on a crystal of maximum length of about 1 mm, with an inclination automatic diffractometer DAR-UM (ref.[26]) (MoK_α radiation; graphite monochromator). No absorption correction was made. The systematic extinction of the reflexions led unequivocally to the space group $P2_12_12_1$.

The structure was determined by direct methods in an automatic regime Rentgen-75 (ref.[27]). The phase problem was elucidated with 650 triplets, including the 111 strongest structural amplitudes $|Ehkl|$. The statistically best set of bases led to the *E* synthesis in which the 11 strongest peaks corresponded to the positions of the non-hydrogen atoms. The assumed structural formula *III* enabled to distinguish the two oxygen atoms and nine carbon atoms already at this stage. Structure refinement by least squares method with neglect of hydrogen atoms in the isotropic approximation of thermal vibrations of non-hydrogen atoms (ref.[28]) reduced the *R* factor to 11·1%. In the further treatment, anisotropic thermal vibrations of the non-hydrogen atoms were included. The differential syntheses of electron densities, together with taking into account the general laws in the placement of hydrogen atoms in organic molecules, allowed to localize all the 12 hydrogen atoms in the molecule. Final structural refinement by the least squares method converged to the weighted discrepancy factor $R_w = 6{\cdot}5\%$. The atom coordinates are given for the 1*S* enantiomer in Table V, thermal vibration data in Table VI, interatomic distances in Table VII and bond angles in Table VIII. The numbering of the atoms follows from Fig. 3, the packing in the unit cell is depicted in Fig. 4.

(2*S*,5*S*)-5-Hydroxybicyclo[2,2,2]octane-2-carboxylic Acid ((+)-*VIb*)

Monomethyl ester of (2*S*,5*S*)-*endo*,*endo*-bicyclo[2,2,2]octane-2,5-dicarboxylic acid ((+)-*IVb*; 2·06 g; 9·72 mmol), prepared from (+)-*IVa* ([α]D +125°) according to ref.[15,17], was dissolved in thionyl chloride (8 ml) and stirred at room temperature for 1·5 h. After evaporation in vacuo the residue was dissolved in ether (2 ml) and the solution was added under nitrogen at 0°C to a vigorously stirred solution of $LiCu(CH_3)_2$, prepared by addition of 1·8M methyl lithium (11·7 ml; 21 mmol) to copper iodide (2·0 g; 10·5 mmol) in ether (10 ml). After 10 min, the stirred mixture was decomposed with a saturated ammonium chloride solution, extracted with ether, dried and taken down, yielding 1·6 g of crude methyl (2*S*,5*S*)-5-acetylbicyclo[2,2,2]-octane-2-carboxylate

(*V*). Mass spectrum, *m/z*: 210 (M^+), 179 (M − OCH_3), 167 (M − $COCH_3$). A solution of this product (1·6 g; 7·62 mmol) and 85% *m*-chloroperoxybenzoic acid (2·0 g; 9·6 mmol) in dichloromethane (10 ml) was set aside for 2 days at room temperature. The separated *m*-chlorobenzoic acid was filtered, washed with dichloromethane, the filtrate was diluted with ether, extracted with 2% sodium hydroxide solution, dried and taken down. Chromatography of the residue on silica gel in pentane–ether (2 : 1) afforded 1·29 g of methyl (2*S*,5*S*)-5-acetoxybicyclo[2,2,2]octane-2-carboxylate (*VIa*), b.p. 109°C/13 Pa. IR spectrum, cm^{-1}: 1 740, 1 236 sh, 1 250 ($OCOCH_3$); 1 725 sh, 1 172, 1 198 ($COOCH_3$). Mass spectrum, *m/z*: molecular ion not present, 183 (M − CH_3CO), 166 (M − CH_3COOH); for $C_{10}H_{14}O_2$ calculated: 166·1002, found: 166·0994. The acetoxy ester *VIa* (1·1 g) was dissolved in a solution of sodium hydroxide (2·3 g) in 50% ethanol (20 ml) at 40°C. After standing for 1 h, ethanol was evaporated *in vacuo*, the aqueous solution was extracted with ether and acidified with conc. hydrochloric acid. The product was taken up in dichloromethane, the extract was dried and taken down, leaving 0·7 g of the hydroxy acid (+)-*VIb*, m.p. 140—142°C, unchanged after crystallization from ethyl acetate; $[\alpha]_D^{20}$ +84·1° (*c* 0·4, ethanol). For $C_9H_{14}O_3$ (170·2) calculated; 63·51% C, 8·29% H; found: 63·74% C, 8·28% H.

TABLE V

Atom coordinates for the (1*S*)-enantiomer of III (Standard deviations in parentheses)

Atom	*x/a*	*y/b*	*z/c*
O_1	0·6178(2)	0·5431(2)	0·3764(4)
O_2	0·5250(2)	0·5075(2)	0·6670(4)
C_1	0·6466(2)	0·9159(3)	0·3821(5)
C_2	0·5459(2)	0·8210(3)	0·3983(4)
C_3	0·5750(2)	0·7336(3)	0·5932(4)
C_4	0·7442(2)	0·8220(3)	0·4320(5)
C_5	0·5431(3)	0·7352(3)	0·2039(5)
C_6	0·5678(2)	0·5867(3)	0·5512(4)
C_7	0·6448(3)	0·6440(3)	0·2157(5)
C_8	0·7032(3)	0·7643(3)	0·6387(5)
C_9	0·7546(3)	0·7159(3)	0·2631(5)
H_1	0·8130(4)	0·8710(5)	0·4570(8)
H_2	0·8550(5)	0·6450(5)	0·2970(8)
H_3	0·7740(4)	0·7430(5)	0·156(8)
H_4	0·549(4)	0·798(5)	0·088(7)
H_5	0·648(4)	0·987(5)	0·500(9)
H_6	0·473(4)	0·686(5)	0·194(9)
H_7	0·473(4)	0·880(5)	0·403(8)
H_8	0·643(4)	0·594(5)	0·095(8)
H_9	0·657(4)	0·951(5)	0·244(8)
H_{10}	0·744(4)	0·674(5)	0·691(8)
H_{11}	0·529(4)	0·753(4)	0·708(8)
H_{12}	0·703(4)	0·837(5)	0·756(7)

TABLE VI

Thermal vibration ellipsoides of non-hydrogen atoms in the molecule of *III*

Atom	Elipsoide axes	Axis length nm	Angles (grad) between ellipsoide axes and crystallographic axes		
			(*ai*)	(*bi*)	(*ci*)
$O_{(1)}$	1	0·027	14	91	76
	2	0·025	104	77	19
	3	0·018	94	167	78
$O_{(2)}$	1	0·032	88	121	31
		0·027	14	77	84
		0·018	104	34	60
$C_{(1)}$	1	0·025	38	87	53
		0·023	120	120	45
		0·018	110	30	69
$C_{(2)}$	1	0·022	75	127	41
		0·020	155	83	66
		0·016	71	37	59
$C_{(3)}$	1	0·020	29	106	66
	2	0·019	73	17	88
	3	0·018	113	85	24
$C_{(4)}$	1	0·025	94	88	05
	2	0·023	53	37	89
	3	0·017	37	127	86
$C_{(5)}$	1	0·027	132	128	64
	2	0·022	125	38	77
	3	0·019	62	84	29
$C_{(6)}$	1	0·023	116	117	39
	2	0·020	31	118	78
	3	0·017	74	41	53
$C_{(7)}$	1	0·027	9	90	81
	2	0·023	95	36	54
	3	0·017	97	126	37
$C_{(8)}$	1	0·026	136	124	66
	2	0·022	103	42	51
	3	0·018	49	111	49
$C_{(9)}$	1	0·025	52	75	41
	2	0·025	74	163	84
	3	0·019	138	98	49

The racemic hydroxy acid m.p. 140—142°C, was prepared in exactly the same way and proved to be identical with a sample prepared according to the literature[16].

TABLE VII

Interatomic distances in the molecule of *III*

Bond	Length, nm	Bond	Length, nm	Bond	Length, nm
C_1C_4	0·1521	C_4C_8	0·1519	C_7C_9	0·1510
C_1C_2	0·1524	C_4C_9	0·1522	C_7O_1	0·1478
C_1H_5	0·104	C_4H_1	0·095	C_7H_8	0·092
C_1H_9	0·096	C_5H_7	0·1509	C_8H_{10}	0·107
C_2C_3	0·1562	C_5H_4	0·097	C_8H_{12}	0·106
C_2C_5	0·1511	C_5H_6	0·096	C_9H_2	0·096
C_2H_7	0·106	C_6O_1	0·1335	C_9H_3	0·077
C_3C_6	0·1504	C_6O_2	0·1197		
C_3C_8	0·1566				
C_3H_{11}	0·094				

TABLE VIII

Bond angles in the molecule of *III*

Atoms	Angle	Atoms	Angle	Atoms	Angle
$C_2C_1C_4$	101°	$C_7C_5C_2$	106°	$C_8C_3C_2$	104°
$C_2C_1H_9$	112°	$C_2C_5H_4$	104°	$C_6C_3C_8$	106°
$C_2C_1H_5$	114°	$C_2C_5H_6$	111°	$C_6C_3C_2$	113°
$C_4C_1H_9$	109°	$C_7C_5H_4$	113°	$C_8C_3H_{11}$	113°
$C_4C_1H_5$	104°	$C_7C_5H_6$	112°	$C_6C_3H_{11}$	108°
$C_3C_2C_1$	103°	$C_4C_8C_3$	103°	$C_2C_3H_{11}$	112°
$C_3C_2C_5$	111°	$C_4C_8H_{10}$	117°	$O_1C_7C_9$	112°
$C_1C_2H_7$	106°	$C_3C_8H_{12}$	106°	$O_1C_7C_5$	107°
$C_3C_2H_7$	118°	$C_3C_8H_{10}$	108°	$C_9C_7C_5$	114°
$C_5C_2H_7$	109°	$C_4C_8H_{12}$	110°	$O_1C_7H_8$	102°
$C_8C_4C_1$	100°	$C_7C_9C_4$	114°	$C_5C_7H_8$	105°
$C_9C_4C_8$	111°	$C_7C_9H_3$	104°	$C_9C_7H_8$	117°
$C_1C_4H_1$	109°	$C_7C_9H_2$	103°	$C_7O_1C_6$	117°
$C_8C_4H_1$	109°	$C_4C_9H_3$	111°	$O_1C_6C_3$	116°
$C_9C_4H_1$	114°	$C_4C_9H_2$	115°	$O_2C_6C_3$	125°
				$O_1C_6O_2$	119°

(1*S*)-4-Oxatricyclo[4,4,0,$0^{3,8}$]decan-5-one ((−)-*II*)

A mixture of the hydroxy acid (+)-*VIb* from the previous preparation (500 mg; $[\alpha]_D^{20}$ +84·1°) and *p*-toluenesulfonic acid (50 mg) in toluene (50 ml) was refluxed for 1 h during which time

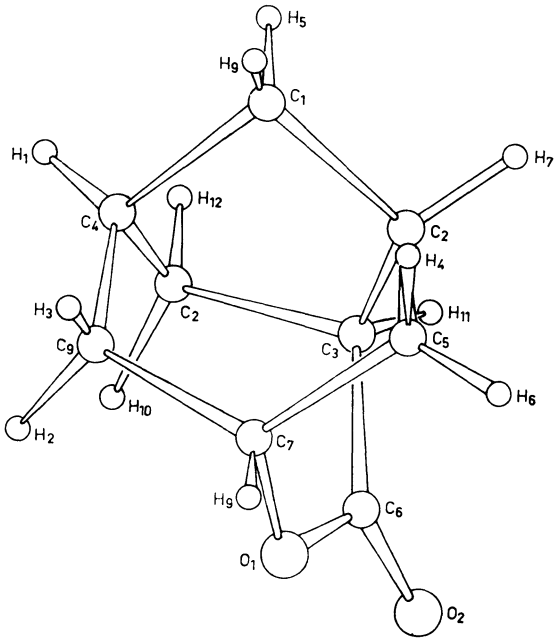


FIG. 3

X-Ray structure of the lactone *III* and the numbering of atoms

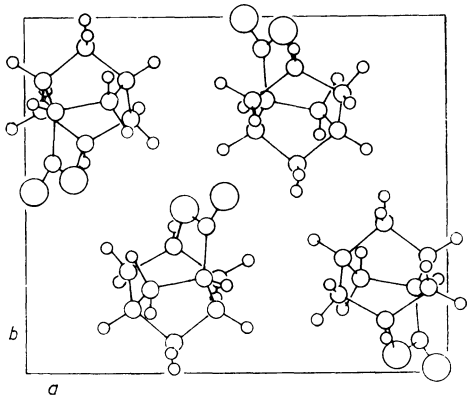


FIG. 4

The packing of molecules of the lactone *III* in the unit cell (projection along the *c* axis)

a part of the toluene (about 3 ml) was very slowly distilled off. The reaction mixture was diluted with ether, extracted twice with sodium hydrogen carbonate solution, dried over sodium sulfate and taken down. The product was chromatographed on a silica gel column (40 g) using a benzene–ether mixture (2 : 1) as eluant. Sublimation in vacuo yielded 206 mg of the pure product (−)-*II*, m.p. 208–209°C; $[\alpha]_D^{20}$ −254·7° (*c* 0·3, benzene). For $C_9H_{12}O_2$ (152·2) calculated; 71·03% C, 7·95% H; found: 71·36% C, 7·98% H. IR spectrum ($CHCl_3$): 1 752 cm^{-1} (6-membered lactone). The same procedure was used for the preparation of the racemic lactone, m.p. 208 to 209°C, undepressed on admixture with an authentic sample (for the racemic compound reported[16] m.p. 204·5–205·5°C; ν(C=O) 1 750 cm^{-1}).

(2*R*)-*endo*-Bicyclo[2,2,2]oct-5-ene-2-carboxylic Acid ((+)-*VII*)

The racemic acid (47 g) was resolved by crystallization of its salts with (+)-3-(4-nitrophenyl)-2-amino-1,3-propanediol (66 g) from aqueous methanol (methanol–water 1 : 5), essentially as described by Červinka[21]. Two crystallizations, followed by decomposition with dilute hydrochloric acid, gave 13 g (55%) of pure acid (+)-*VII*, m.p. 46–47°C, $[\alpha]_D^{22}$ +52·2° (*c* 0·5, methanol) (reported[17] m.p. 46–47°C, $[\alpha]_D^{25}$ +50·9° (*c* 0·45, methanol).

(3*S*)-4-Oxatricyclo[4,3,1,$0^{3,7}$]decan-5-one ((+)-*I*) and
(3*R*)-5-Oxatricyclo[4,3,1,$0^{3,8}$]decan-4-one ((+)-*III*)

The lactonization of the acid (+)-*VII* was carried out essentially as described by Moriarty and coworkers[18]. A sclution of (+)-*VII* ($[\alpha]_D^{20}$ +52·2° (*c* 0·5, methanol); 2·0 g) in 96% H_2SO_4 was allowed to stand at 20°C for 5 min, decomposed with ice and extracted several times with dichloromethane. The combined extracts were washed with sodium hydrogen carbonate solution and water, dried and taken down. Chromatography of the residue on silica gel (300 g; benzene–ether 3 : 1) afforded 0·21 g of (+)-*I*, m.p. 203–204°C (methylcyclohexane); $[\alpha]_D^{22}$ +8·1° (*c* 0·5, methanol); reported[24] m.p. 202·5–203·5°C and $[\alpha]_D^{16}$ +8·4°. After a middle fraction the lactone (+)-*III* (0·9 g) was collected; m.p. 235–236°C (methylcyclohexane), $[\alpha]_D^{22}$ +23·1 (*c* 0·5, methanol). For $C_9H_{12}O_2$ (152·2) calculated: 71·03% C, 7·95% H; found: 70·89% C, 7·99% H. The IR spectra of (+)-*I* and (+)-*III* were identical with those of the racemic lactones.

(4*S*)-5-Oxatricyclo[5,2,1,$0^{4,8}$]decan-6-one ((−)-*VIII*)

A solution of the acid (+)-*VII* ($[\alpha]_D^{22}$ +49·0° (*c* 0·5, methanol)); (1·0 g) in 96% sulfuric acid (10 ml) was set aside at 25°C for 8 h. The mixture was worked up as described in the preceding experiment and the product was repeatedly chromatographed on silica gel in benzene–ether (3 : 1), affording 85 mg of the lactone (−)-*VIII*. After sublimation in vacuo and crystallization from ether (−70°) the compound melted at 175–178°C; $[\alpha]_D^{22}$ −39·6° (*c* 0·26, dichloromethane). Its IR spectrum was identical with that of the racemic compound. For $C_9H_{12}O_2$ (152·2) calculated: 71·03% C, 7·95% H; found: 71·15% C, 7·89% H.

(3*S*)-4-Oxatricyclo[4,3,1,$0^{3,7}$]decan-5-one ((+)-*I*)

The acid (+)-*VII* ($[\alpha]_D^{22}$ +49·8° (*c* 0·5, methanol); 1·0 g) was converted into the iodo lactone (−)-*XIII*, m.p. 116–117°C (ethyl acetate), $[\alpha]_D^{22}$ −97·7° (*c* 1, $CHCl_3$) in the same way as described; yield 1·7 g (92·9%). (For the other enantiomer reported m.p. 116°C, $[\alpha]^{25}$ +119° (*c* 1, methanol)). Reduction of the iodo lactone (1·0 g) in ethyl acetate (15 ml) over Adams catalyst (50 mg) in the presence of triethylamine (0·5 ml) gave 320 mg (58%) of the lactone (+)-*I*, m.p. 207–208°C (methylcyclohexane); [θ] (222·5 nm) +2 900 (ethanol).

Racemization of Lactone (+)-*III*

A solution of the acid (+)-*VII* (4·0 g; $[\alpha]_D^{22}$ +49° (*c* 0·5, methanol)) in 96% sulfuric acid (40 ml) was kept at 20°C. After 30 min, 15 ml of the solution was withdrawn and decomposed with ice. The products were taken up in dichloromethane and the organic layer was washed with sodium hydrogen carbonate solution and water. After evaporation of the solvent, the lactone (+)-*III* was separated by repeated chromatography on silica gel in hexane–ether (2 : 1), sublimed and its CD spectrum was taken in ethanol, $\theta = +8\,700$. Another sample was taken after 8 h, $\theta = +7\,500$. The remaining solution was worked up after 120 h, the θ value being +5 700.

Degradation of Lactone (+)-*III* to Ketone (−)-*XI*

The whole reaction sequence was carried out essentially as described for the racemic material[18]. The lactone (+)-*VI* ($[\alpha]_D^{22}$ +23·1°; 1·97 g, 13 mmol) was dissolved in 1M-NaOH (13 ml) and water (37 ml) with warming. Ruthenium dioxide hydrate (25 mg) was added to the cold solution. Sodium periodate (2·9 g) in water (25 ml) was then added in portions under stirring. After destroying the excess ruthenium tetroxide, the mixture was acidified and extracted five times with ethyl acetate. The usual work-up procedure gave 1·7 g (78%) of the crude keto acid (+)-*IX* which after crystallization from ether melted at 170–172°C; $[\alpha]_D^{22}$ +37·3° (*c* 0·3 chloroform). Its IR spectrum was identical with that of the racemic acid.

A mixture of (+)-*IX* (1·0 g), sodium hydroxide (0·5 g), 85% hydrazine hydrate (1 ml) and diethylene glycol (8 ml) was refluxed for 1 h. The condenser was removed until the temperature rose to 200–210°C and the mixture was refluxed at this temperature for 3 h. Extraction with benzene, followed by sublimation at 50°C/25 Pa, afforded 680 mg (74%) of (+)-*X*, m.p. 75–77°C; $[\alpha]_D^{22}$ +38° (*c* 0·5, chloroform); IR spectrum identical with that of the racemic acid.

The acid (+)-*X* (650 mg) was converted into its methyl ester with diazomethane in ether; yield 700 mg (99%) of an oil; $[\alpha]_D^{22}$ +34° (*c* 0·5 chloroform). A solution of the ester (600 mg; 3·75 mol) in ether (4 ml) was added dropwise during 10 min to an ice-cooled solution of Grignard reagent, prepared from 0·7 g of magnesium and 4·32 g of bromobenzene in ether (10 ml). Cooling and stirring was continued for 10 min and then the mixture was allowed to stand for 45 min at room temperature. After decomposition with 6M-HCl, the crude alcohol was extracted into ether (3 × 15 ml). The ethereal extracts were combined, washed with sodium hydroxide solution, water, dried over sodium sulfate and taken down, leaving 980 mg of the crude product. Chromatography of silica gel in ether–light petroleum (1 : 4) afforded the crystalline alcohol (750 mg; 72%), melting at 96–97°C. Mass spectrum: 292 (M^+), 274, 215, 183, 105; IR spectrum identical with that of the racemic compound.

A mixture of the optically active alcohol (0·6 g), benzene (50 ml), *p*-toluenesulfonic acid hydrate (0·08 g) and anhydrous calcium chloride (0·3 g) was refluxed for 1·5 h, cooled and filtered. The filtrate was washed with sodium hydrogen carbonate solution, water, dried and taken down in vacuo to give 0·56 g of a solid which was purified by chromatography on silica gel in ether–light petroleum (1 : 50); yield 0·51 g of pure compound, m.p. 95–97°C, whose IR and mass spectrum was identical with those of the racemic product. A solution of sodium periodate (0·4 g) in water (10 ml) was added to a shaken mixture of ruthenium dioxide (10 mg) and tetrachloromethane at 10°C (20 ml). To the yellow mixture a solution of the optically active olefin (200 mg) from the preceding experiment in tetrachloromethane (5 ml) was added. The mixture was shaken for 2 h, the organic layer was separated and the aqueous one was extracted with three portions of ether. The usual work-up procedure afforded an oil which was sublimed at 25°C/1·3 kPa to give 20·5 mg of a waxy solid, m.p. 141–143°C; pure according to thin-layer chromatography. Mass spectrum: 124 (M^+), 95, 81, 80, 67, 54, 41 (reported[18] for the racemic compound: 124, 81, 80, 67, 54, 41). CD spectrum (ethanol): $\theta = 6\,100$ (ν = 302 nm).

Semicarbazone: m.p. 189–191°C; $[\alpha]_D^{22}$ +27·8° (*c* 0·18, chloroform) (reported[19] for the other enantiomer: m.p. 188–189°C, $[\alpha]_D^{17}$ −31·6° (*c* 0·63, chloroform).

Equilibration of Lactones *I*, *III* and *VIII*

The ground lactone (100 mg) was dissolved in 96% sulfuric acid (5 ml) with stirring and the solution was kept at 25°C in a thermostate. At appropriate time intervals, 0·15 ml samples were withdrawn which were decomposed with ice (4 g) and extracted with dichloromethane (2 ml). The extract was washed with saturated sodium hydrogen carbonate solution and water (1ml each), taken down and the residue analyzed by gas–liquid chromatography. For the kinetic graphs see Fig. 1.

endo-2-Iodo-4-oxatricyclo[4,3,1,$0^{3,7}$]decan-5-one (*XIV*)

A solution of the racemic iodo lactone *XIII* (ref.[22], m.p. 79–81°C; 2·8 g) and triethylamine (1·4 ml) in ethyl acetate (50 ml) was hydrogenated over PtO_2 (50 mg). After consumption of 140 ml of hydrogen the hydrogenation was interrupted, the mixture filtered, diluted with ether, washed with dilute hydrochloric acid and water, dried over sodium sulfate and taken down. The residue (1·8 g) was chromatographed on a column of silica gel (100 g) in ether–light petroleum (1 : 1). The first fraction furnished 0·7 g of the starting iodo lactone *XIII*, m.p. 79–81°C. After a middle fraction, containing predominantly the lactone *I*, the iodo lactone *XIV* was eluted; m.p. 108 to 109°C (ethyl acetate); yield 210 mg. IR spectrum (chloroform): 1 780 cm^{-1}. For $C_9H_{11}IO_2$ (278·1) calculated: 38·87% C, 3·99% H, 45·63% I; found: 38·95% C, 3·77% H, 45·06% I. ^1H NMR spectrum: see Table III. Mass spectrum *m/z*: 278 (M^+), 151 (M-I), 128 (HI), 127 (I), 107 (151-CO_2) 95, 79, 67.

Hydrogenation of *XIV* (330 mg) in ethyl acetate (15 ml) in the presence of triethylamine (0·2 ml) and platinum oxide (50 mg) afforded 140 mg (77%) of the lactone *I*, m.p. 206–207°C, identical in all respects with an authentic[18,23] compound.

Isomerization of the Iodo Lactones *XIII* and *XIV*

Platinum oxide (50 mg) was reduced in ethyl acetate (5 ml). The racemic iodo lactone *XIII* or *XIV* (100 mg), followed by triethylamine (0·1 ml) was added and the mixture was hydrogenated. When 5 ml of the hydrogen had been absorbed (about 5 min), the hydrogenation was interrupted, the mixture filtered, extracted with dilute hydrochloric acid and water, dried and taken down *in vacuo*. Thin-layer chromatography in ether–light petroleum 2 : 1 showed the spots due to *XIII*, *I* and *XIV*. Quantitative analysis by ^1H NMR spectroscopy showed that both *XIII* and *XIV* gave the same mixture in which the ratio *XIII* : *XIV* was 2 : 1. Isomerization attempts in the presence of pre-reduced platinum (with or without triethylamine for 7 h at 40°C under nitrogen) or even hydrogenation in the absence of triethylamine, were unsuccessful.

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