

## REACTIVITY OF 1-CYCLOPROPENE-1-LACTONES DEPENDENT ON THE SUBSTITUTION DEGREE

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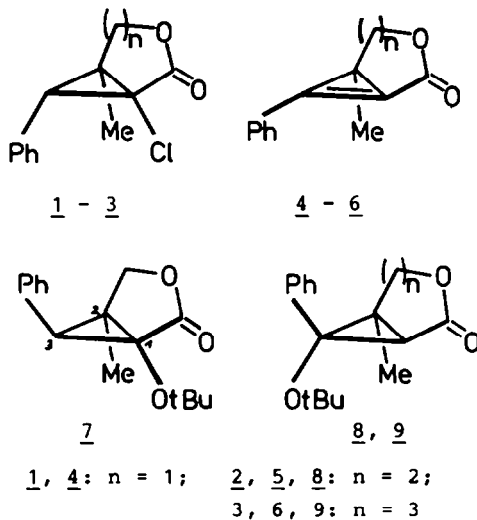
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**ABSTRACT** - Reaction of the  $\alpha$ -chloro lactone 10 with KOtBu gives the butoxy lactones 21 and 22; the seven-membered derivative 11 leads to 23 as the only isolable product. Formation of the  $\alpha$ -substitution product 21 as well as the enhanced instability of the intermediates 12 and 13 in comparison to their methyl substituted homologues 5 and 6 show the kinetical stabilization by a methyl group at C-2. Products derived from a cyclopropeno lactone of type A could not be detected.

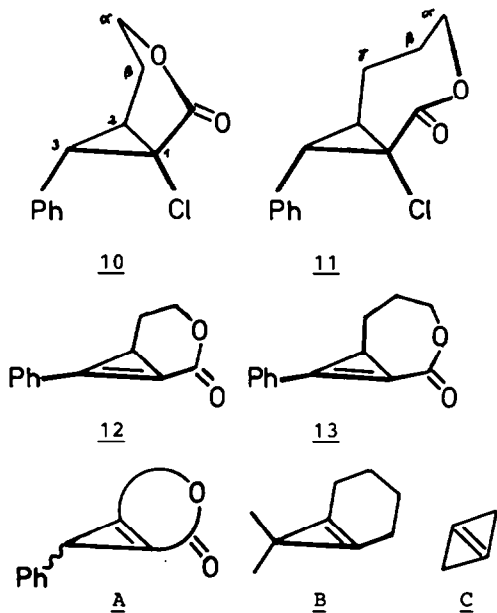
### Introduction

As we have shown previously [2,3] the bicyclic  $\alpha$ -chlorolactones 1-3 react with KOtBu in THF to give the t-butoxy lactones 7-9 via the highly strained cyclopropeno lactones 4-6. The reaction path changed with the size of the anellated lactone ring. The extremely strained intermediate 4 with a calculated (MINDO/3) [3] interplanar angle of  $40^\circ$  adds the t-butoxy anion to the bridgehead to give the more stable benzylic anion leading to 7. That means 4 does not react as an  $\alpha,\beta$ -unsaturated lactone which is to add nucleophiles to the  $\beta$ -position, but because there is almost no conjugation its behaviour is comparable to that of a very unstable simple cyclopropene not influenced by the lactone group. The less strained 5 also can not be isolated, but it reacts in a normal way at the  $\beta$ -standing C-atom to give 8 (and its isomer with changed positions of the substituents at C-3). Finally the isolated seven-membered lactone 6 is fairly stable but it can be converted very rapidly to 9 (and its isomer). In all these cases we started from chloro lactones bearing

a methyl group at C-2, because previous results [4] showed that the stability of the cyclopropene carboxylic derivatives is greatly enhanced by a higher substitution degree at C-2.



Now we wish to report the reaction of KOtBu with the chloro lactones 10 and 11, derivatives without methyl group at C-3. Our main interest was focussed on the behaviour of the cyclopropeno lactones 12 and 13. Would they be isolable, at least 13 analogously to 6? Would the addition of t-butanol run



similarly to that on 5 and 6? Would subsequent products of an isomeric lactone of type A be detected? Such compounds should not be formed by rearrangement of the lactones 12 or 13 via a cyclopropenyl anion [5] but on a former stage chloride elimination could take place by H-shift leading to the presumably thermodynamically more stable cyclopropene A. Indications to such a possible reaction pathway might be the isolation of cyclopropenes of type B [6], and calculations that bicyclobutenes of type C represent a local minimum on the  $C_4H_4$  potential energy hypersurface [7].

#### Synthesis of 10 and 11

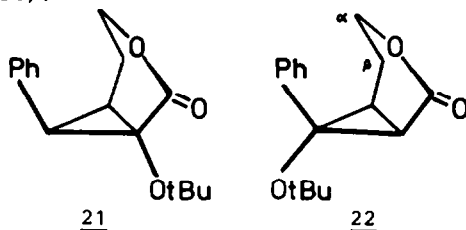
The synthesis of 10 and 11 was accomplished in a similar way as described previously for 2 and 3 [3]. Reduction of the ester 14 with  $LiAlH_4$  to the alcohol 15 and a one-pot reaction with dihydropyran followed by phase transfer catalyzed  $CCl_2$ -addition gave 19. Treatment with  $BuLi$ , subsequent carboxylation, and ring closure of the intermediate hydroxy carboxylic acid led to the lactone 10. Starting from the malonate 16 via the carboxylic acid 17

and the alcohol 18 the homologous derivative 20 could be obtained. The  $^1H$ -NMR spectra for both the chloro lactones are remarkable. The situation in the lactone ring of 10 and 11 is comparable with that of the methylated derivatives 2 and 3 including the extremely different  $\gamma$ -protons of 11 ( $\delta = 2.56$  and  $1.09$ ) [3]. The downfield shift of the proton at C-2 of 10 ( $\delta = 2.57$ ) is surprising for such a cyclopropane-H, particularly in comparison to the same proton of 11 with  $\delta = 1.83$ . This difference of  $0.74$  ppm is nearly the same as for both the 3-H of 10 ( $3.29$ ) and 11 ( $2.53$ ).

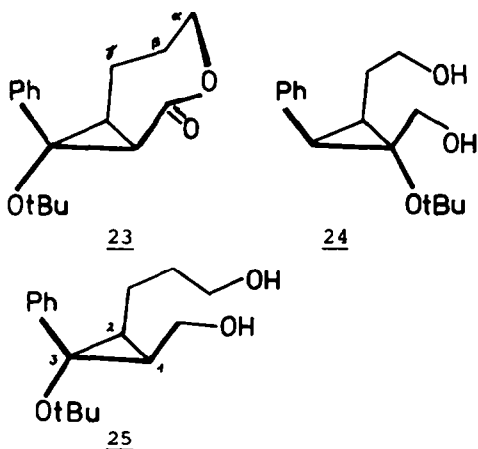
	R
	<u>14</u> COOMe
<u>14 - 18</u>	<u>15</u> $CH_2OH$
	<u>16</u> $CH(COOEt)_2$
	<u>17</u> $CH_2COOH$
	<u>18</u> $CH_2CH_2OH$
	<u>19</u> $CH_2OTHP$
	<u>20</u> $CH_2CH_2OTHP$

#### Reaction of 10 and 11 with $KOtBu$

Treatment of chlorolactone 10 with  $KOtBu$  in THF at  $0^\circ C$  gave two separable *t*-butoxy lactones 21 (40%) and 22 (23%).



The structure of the unexpected lactone 21 can be deduced from the  $^1H$ -NMR spectrum with the doublet  $\delta = 2.99$  ( $J = 10$  Hz) for the 3-H, and an AB-system  $3.87, 2.93$  with one strongly upfield shifted proton of the  $\alpha$ - $CH_2$ -group of the lactone ring caused by the shielding effect of the *cis* phenyl ring. Final evidence for the structure was given by reduction of 21 with  $LiAlH_4$  to the diol 24. The uncoupled



AB system of the  $\text{CH}_2\text{OH}$  group at C-1, and a doublet ( $\delta = 2.66$ ) for the 3-H clearly indicated the substitution pattern. The normal addition product 22 showed an unusual small coupling constant of 5 Hz for cis-standing cyclopropane protons, but all other data are in a good agreement with the spectrum of the homologous compound 8 [3]. Other compounds than 21 and 22 could not be isolated, although small amounts of the isomer of 22 (Ph and tBuO exchanged) seem to be present ( $^1\text{H-NMR}$ ). The formation of a product derived from the lactone of type A can be ruled out. Experiments with less amounts of  $\text{KOtBu}$  show that also from 10, similarly to the reaction of 2, traces of the unstable intermediate 12 can be seen by both IR ( $1810\text{ cm}^{-1}$ ) and  $^1\text{H-NMR}$  spectra ( $\delta = 7.7$ ).

From 11 with  $\text{KOtBu}$  only one product, the butoxy derivative 23 could be isolated in more than 50% yield. Again the primary product 13 could only be detected as a short living species by IR and  $^1\text{H-NMR}$  spectra. Unfortunately, some by-products formed in small amounts are completely unseparable, but inspection of the  $^1\text{H-NMR}$  spectrum of this mixture showed that a lactone of type A as well as its reaction product with  $\text{KOtBu}$  should not be present.

The structure of 23 was again elucidated by the reduction to diol 25.

Here a doublet of an AB system is typical for the  $\text{CH}_2\text{OH}$  group at C-1.

#### Conclusion

The elimination-addition reaction of the chloro lactones 10 and 11 in comparison to the homologues 2 and 3 shows that the more simple systems 10 and 11 are less stable. Formation of the  $\alpha$ -t-butoxy derivative 21 from 10 reminds of the reaction of the five-membered ring lactone 1 ( $\rightarrow$  7). That means, the reaction pathway of the intermediate 12 is comparable to that of 4, the most strained system in these series.

In addition 13 must be much more unstable than the homologue 6, which could be isolated and fully characterized.

Because presumably the ring strain of the cyclopropeno lactones might not be influenced by a methyl group at C-2, obviously a kinetical stabilization is given by the methyl group. The nearly exclusive formation of the endo-phenyl isomers (22, 23) show the facilitated attack of the t-butoxy anion from the exo-side by absence of the methyl group.

The lack of any products derived from a lactone of type A might be explained by the conjugation with the phenyl ring. Further experiments with other groups than phenyl at C-3 are under investigation.

#### EXPERIMENTAL

$^1\text{H-NMR}$  spectra: in  $\text{CDCl}_3$ ; Bruker WH-400 (TMS,  $\delta = 0$  ppm). -  $^{13}\text{C-NMR}$  spectra: in  $\text{CDCl}_3$ ; off resonance; Varian CFT-20; signals for phenyl and olefin C are not published. - IR-spectra: Perkin-Elmer 257. - MS: Varian-MAT 711 (70 eV). - The m.ps and b.ps are uncorrected. - For kugelrohr distn (KRD) all temp. mean the air bath. - Column chromatography (CC) on silica gel (desactivated with 3% water) with petroleum ether/ether (PE/E). - All organic phases were dried over  $\text{MgSO}_4$ .  
Methyl (E)-4-phenyl-3-butenoate (14)  
 According to ref. [8] a mixture of 38.0 g (0.30 mol) of benzyl chloride

55.5 g (0.30 mol) of tributylamine, 32.3 g (0.375 mol) of methyl acrylate, and 0.675 g of anhydrous palladium acetate was stirred at 110 °C for 15 hrs. After cooling it was acidified with cold dil. HCl and extracted with ether. Evaporation of the solvent and fractional distn gave 34.5 g (65%) of 14, b.p. 108-110 °C/3 torr. -  $^1\text{H-NMR}$ :  $\delta$  = 3.29 (dd,  $J$  = 7; 1.5 Hz; 2-H), 3.74 (s; OMe), 6.34 (dt,  $J$  = 16; 7 Hz; 3-H), 6.53 (d, br.,  $J$  = 16 Hz; 4-H), 7.24, 7.32, 7.38 (ABB'CC' system,  $J_{AB} = J_{BC} = 7$ ,  $J_{AC} = 1$  Hz; p-, m-, o-H). lit. [9] 3.25 (d), 3.7 (s), 5.9-6.3 (m), 6.57 (d), 7.33 (s). -  $^{13}\text{C-NMR}$ :  $\delta$  = 38.2 (t; C-2), 51.7 (q; OMe), 171.8 (s; C-1).

(E)-4-Phenyl-3-buten-1-ol (15)

To a stirred slurry of 5.58 g (0.15 mol) of  $\text{LiAlH}_4$  in 150 ml of ether at 0 °C, a soln of 26.4 g (0.15 mol) of 14 in 100 ml of ether was added slowly. After further stirring for 1 hr at 0 °C and 30 min at room temp. the mixture was worked up as usual with ice/dil.  $\text{H}_2\text{SO}_4$  and distilled to afford 22.1 g (99%) of 15, b.p. 60 °C/0.04 torr (KRD), m.p. 34 °C (lit. [10] 35 °C). -  $^1\text{H-NMR}$ :  $\delta$  = 2.55 (dtd,  $J$  = 7; 6; 1 Hz; 2-H), 3.78 (t,  $J$  = 6 Hz; 1-H), 6.26 (dt,  $J$  = 15.5; 7 Hz; 3-H), 6.55 (d, br.,  $J$  = 15.5 Hz; 4-H), 7.24, 7.32, 7.38 (ABB'CC' system,  $J_{AB} = J_{BC} = 7$ ,  $J_{AC} = 1$  Hz; p-, m-, o-H). -  $^{13}\text{C-NMR}$ :  $\delta$  = 36.3 (t; C-2), 61.9 (t; C-1).

Diethyl (E)-3-phenyl-2-propenylpropanedioate (diethyl cinnamylmalonate) (16)

Prepared from diethyl malonate and cinnamyl chloride according to lit. [11], b.p. 100-103 °C/0.05 torr (lit. [11] 137-140 °C/0.1 torr). -  $^1\text{H-NMR}$ :  $\delta$  = 1.41 (t,  $J$  = 7 Hz; 2 Me), 2.81 (ddd,  $J$  = 7; 7; 1.5 Hz; 1'-H), 3.50 (t,  $J$  = 7 Hz; 2-H), 4.20, 4.21 (ABq,  $J$  = 11; 7 Hz; 2  $\text{CH}_2\text{O}$ ), 6.19 (dt,  $J$  = 15; 7 Hz; 2'-H), 6.50 (d, br.,  $J$  = 15 Hz; 3'-H), 7.2-7.4 (m; Ph). -  $^{13}\text{C-NMR}$ :  $\delta$  = 14.1 (q; 2 Me), 32.3 (t; C-1'), 52.1 (d; C-2), 61.4 (t;  $\text{CH}_2\text{O}$ ), 168.9 (s; C-1, -3).

(E)-5-Phenyl-4-pentenoic acid (17)

A mixture of 16.6 g (60 mmol) of 16 in 40 ml of ethanol and 12 g of KOH in 15 ml of water was refluxed for 4 hrs. After removing most of the solvent the residue was dissolved in water and acidified with conc. HCl under ice cooling. The mixture was extracted with ether and evaporated. The residue was heated in a distn flask up to 170-180 °C/15 torr. Under evolution of  $\text{CO}_2$  8.1 g (77%) of 17 were collected, which solidified spontaneously, m.p. 88 °C (lit. [12] 90 °C). -  $^1\text{H-NMR}$ :  $\delta$  = 2.60, 2.61 ( $\text{A}_2\text{B}_2$  system; 2-, 3-H), 6.24 (dt,  $J$  = 15; 6.5 Hz; 4-H), 6.46 (d, br.,  $J$  = 15 Hz; 5-H), 7.22, 7.31, 7.35 (ABB'CC' system,

$J_{AB} = J_{BC} = 7$ ,  $J_{AC} = 1$  Hz; p-, m-, o-H). -  $^{13}\text{C-NMR}$ :  $\delta$  = 27.9 (t; C-2), 33.8 (t; C-3), 179.6 (s; COOH).

(E)-5-Phenyl-4-penten-1-ol (18)

A soln of 16.0 g (91 mmol) of 17 in 100 ml of THF was added dropwise to a stirred slurry of 4.9 g (130 mmol) of  $\text{LiAlH}_4$  in 150 ml of THF at 0 °C. After 30 min it was slowly warmed to reflux temp. and maintained refluxing for 2 hrs. After usual work-up with ice/dil.  $\text{H}_2\text{SO}_4$  distn afforded 13.1 g (89%) of 18, b.p. 132-135 °C/4 torr (lit. [13] 112-113 °C/1 torr).  $^1\text{H-NMR}$ :  $\delta$  = 1.80 (tt,  $J$  = 6.5; 6.5 Hz; 2-H), 2.33 (dtd,  $J$  = 6.5; 6.5; 1 Hz; 3-H), 3.72 (t,  $J$  = 6.5 Hz; 1-H), 6.35 (dt,  $J$  = 15; 6.5 Hz; 4-H), 6.43 (d, br.,  $J$  = 15 Hz; 5-H), 7.21, 7.30, 7.35 (ABB'CC' system,  $J_{AB} = J_{BC} = 7$ ,  $J_{AC} = 1$  Hz; p-, m-, o-H). -  $^{13}\text{C-NMR}$ :  $\delta$  = 29.3 (t; C-2), 32.2 (t; C-3), 62.0 (t; C-1).

Preparation of Dichlorocyclopropanes 19 and 20. General procedure [2].

A mixture of 0.1 mol of 15 resp. 18, 8.4 g (0.1 mol) of dihydropyran and one drop of conc. HCl was stirred for 12 hrs. Then 50 ml of  $\text{CHCl}_3$ , 50 ml of 50% NaOH and 0.2 g of benzyltriethylammonium chloride were added and stirred for further 20 hrs. After usual work-up distn (KRD) gave the products.

2-(2,2-Dichloro-t-3-phenyl-r-1-cyclopropyl)-1-ethanol-tetrahydro-2-pyran-yl ether (19, epimeric mixture)

20.7 g (0.14 mol) of 15 gave 42.3 g (96%) of 19, b.p. 95-100 °C/0.05 torr. -  $^1\text{H-NMR}$ :  $\delta$  = 1.5-2.2 (m; 9 H), 2.52 (d,  $J$  = 8 Hz; 3-H), 3.5-4.0 (m; 4 H), 4.65 (dd,  $J$  = 7.5; 3.5 Hz; 2'-H), 7.2-7.4 (m; Ph). -  $^{13}\text{C-NMR}$ :  $\delta$  = 19.3/19.4 (t; C-4'), 25.5 (t; C-5'), 30.6 (t; C-3'), 30.6 (d; C-1), 32.8 (t; 1- $\text{CH}_2$ ), 40.7 (d; C-3), 61.9/62.1 (t; C-6'), 65.6/65.7 (t; 1- $\text{CH}_2\text{CH}_2\text{O}$ ), 65.9 (s; C-2), 98.7/98.8 (d; C-2'). - Found: C, 60.72; H, 6.27; calcd for  $\text{C}_{16}\text{H}_{20}\text{Cl}_2\text{O}_2$ : C, 60.96; H, 6.40.

2-(2,2-Dichloro-t-3-phenyl-r-1-cyclopropyl)-1-propanol-tetrahydro-2-pyran-yl ether (20, epimeric mixture)

16.2 g (0.10 mol) of 18 gave 30.6 g (93%) of 20, b.p. 110-115 °C/0.1 torr. -  $^1\text{H-NMR}$ :  $\delta$  = 1.5-2.0 (m; 11 H), 2.45/2.46 (2 d,  $J$  = 7.5 Hz; 3-H), 3.5-3.6 (m; 2 H), 3.7-3.9 (m; 2 H), 4.60 (mc; 2'-H), 7.2-7.4 (m; Ph). -  $^{13}\text{C-NMR}$ :  $\delta$  = 19.6 (t; C-4'), 25.5 (t; C-5'), 27.4, 28.6 (2 t; 1- $\text{CH}_2\text{CH}_2$ ), 30.8 (t; C-3'), 35.0 (d; C-1), 41.0 (d; C-3), 62.3 (t; C-6'), 66.2 (s; C-2), 66.8 (t;  $\text{CH}_2\text{O}$ ), 98.9 (d; C-2'). Found: C, 61.88; H, 6.62; calcd for  $\text{C}_{17}\text{H}_{22}\text{Cl}_2\text{O}_2$ : C, 62.01; H, 6.73.

Table 1.  $^1\text{H-NMR}$  data for 10, 11, 21 - 25 (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ )

Compd <sup>a)</sup>	Position		$\beta$		$\gamma_1$	$\gamma_2$	Ot-Bu	$\alpha_1\alpha_2$	$\alpha_1\beta_1$	$\alpha_1\beta_2$	$\alpha_2\beta_1$	$\alpha_2\beta_2$	J [Hz]					
	1	2	$\beta_1$	$\beta_2$	$\gamma_1$	$\gamma_2$		$\alpha_1$	$\alpha_2$	$\alpha_1\beta_1$	$\alpha_1\beta_2$	$\alpha_2\beta_1$	$\alpha_2\beta_2$	$\beta_1\beta_2$	$2,\gamma_1$	$2,\gamma_2$	$2,3$	$2,1$
<u>10</u>	----	2.57	3.29	4.48 <sup>b)</sup> 4.35	2.53 2.19	-----	-----	12	6	1	13	4	14	3.5	-----	7	-----	-----
<u>21</u>	----	2.35	2.99	3.87 <sup>c)</sup> 2.93	2.45 2.11	-----	1.38	12	7	1.5	11.5	4.5	14	4	-----	10	-----	-----
<u>22</u>	2.34	2.62	-----	4.20 3.69	2.37 2.20	-----	1.20	9	9.5	2.5	10	7	12	4.5	-----	5	-----	-----
<u>11</u> <sup>d)</sup>	-----	1.83	2.53	4.88 4.43	2.19 1.90	2.56 1.09	-----	12.5	12	4.5	7	1	14	-----	2	7	-----	-----
<u>23</u> <sup>e)</sup>	2.18	2.36	-----	3.68 3.43	1.60 <sup>f)</sup> 1.60	2.12 <sup>f)</sup>	1.20	10	4 <sup>g)</sup>	3	10 <sup>g)</sup>	4	h)	5 <sup>g)</sup>	-----	7	-----	-----
<u>24</u> <sup>i)</sup>	-----	1.41 <sup>k)</sup>	2.66	3.86 3.82	1.85 1.16	-----	1.47	12	4	8	4	6	14.5	4	-----	10.5	-----	-----
<u>25</u> <sup>l)</sup>	1.68	2.08	-----	3.66 3.43	1.60 <sup>f)</sup> 1.60	1.60 <sup>f)</sup>	1.20	10.5	3.5 <sup>g)</sup>	3	9.5 <sup>g)</sup>	4	h)	-----	6 <sup>g)</sup>	2.5	-----	7.5

a) For all compounds: 7.2-7.4 (m; Ph). - b) W-coupling 1 Hz ( $\alpha,2$ ). - c) W-coupling 1.5 Hz ( $\alpha,2$ ). -

d) J:  $\beta_1\gamma_1 = 1$ ,  $\beta_1\gamma_2 = 7$ ,  $\beta_2\gamma_1 = 6.5$ ,  $\beta_2\gamma_2 = 12$ ,  $\gamma_1\gamma_2 = 13$  Hz. - e) Assignment supported by spin decoupling. -

f) mc. - g) Assignment not possible. - h) J:  $\beta_1\beta_2$  and all  $\beta_1/2\gamma_1/2$  not definable. - i) 4.20, 3.44 (AB-

system, J = 12 Hz;  $\alpha_1'\alpha_2'$ ). - k) W-coupling 1 Hz ( $\alpha_1',2$ ). - l) 3.36, 3.25 (dAB,  $J_{AB} = 11.5$ ,  $J_{1,A} = 6$ ,

$J_{1,B} = 7.5$ ;  $\alpha_1'\alpha_2'$ ).

Table 2  $^{13}\text{C}$ -NMR data for 10, 11, and 21 - 23 (off resonance,  $\text{CDCl}_3$ ,  $\delta$ )

Compound	C-1	C-2 (d)	C-3	C- $\alpha$ (t)	C- $\beta$ (t)	C- $\gamma$ (t)	C=O (s)	tBuO (q; s)
<u>10</u>	45.0 (s)	29.6	31.7 (d)	66.3	20.8	----	167.0	----
<u>21</u>	59.5 (s)	28.0	36.6 (d)	65.4	20.2	----	172.3	78.2; 29.8
<u>22</u>	31.7 (d)	27.2	76.8 (s)	66.9	28.6	----	168.6	80.3; 27.8
<u>11</u>	46.1 (s)	26.6	32.5 (d)	66.5	25.7*	25.2*	168.3	----
<u>23</u>	35.1 (d)	23.0	68.9 (s)	64.1	19.1	21.4	169.1	80.1; 27.8

\* exchangeable

Preparation of the  $\alpha$ -chloro lactones10 and 11 ( $^1\text{H}$ -,  $^{13}\text{C}$ -NMR data see tab.1 and 2). - General procedure [2]

To a soln of 30 mmol of 19 resp. 20 in a mixture of 120 ml of THF, 30 ml of ether and 30 ml of PE were added dropwise under stirring at  $-90$  to  $-100$  °C 30 ml (47 mmol) of 15% BuLi in hexane; after 1 hr at  $-100$  °C about 10 g of freshly crushed dry ice were added and the mixture was allowed to warm up to room temp. Then 100 ml of ether were added and extracted twice with each 150 ml of 2% NaOH. The combined alkaline layers were acidified with 10% HCl and extracted twice with ether. After removal of the solvent the crude hydroxycarboxylic acids were treated as described below.

1-Chloro-c-2-(2-hydroxyethyl)-t-3-phenyl-r-1-cyclopropanecarboxylic acid lactone (10)

25.2 g (80 mmol) of 19 gave a crude product which was treated [3] with p-toluenesulfonic acid to give 3.0 g (17%) of 10, m.p. 113 °C (PE/E). - IR:  $1730\text{ cm}^{-1}$  (CO). - MS: m/e = 222, 224 ( $\text{M}^+$ , 20%), 187 (M - Cl, 60), 128 (100). - Found: C, 64.64; H, 4.90; calcd for  $\text{C}_{12}\text{H}_{11}\text{ClO}_2$ : C, 64.73; H, 4.98.

1-Chloro-c-2-(2-hydroxypropyl)-t-3-phenyl-r-1-cyclopropanecarboxylic acid lactone (11)

16.5 g (50 mmol) of 20 gave a crude product which was treated [3] with 2-chloro-1-methylpyridinium iodide. After CC (PE/E 1:1) 1.54 g (13%) of 11 were obtained, m.p. 54 °C (PE/E). IR:  $1740\text{ cm}^{-1}$  (CO). - MS: m/e = 236, 238 ( $\text{M}^+$ , 70%), 201 (M - Cl, 50), 173 (60), 129 (100). - Found: C, 65.84; H, 5.47; calcd for  $\text{C}_{13}\text{H}_{13}\text{ClO}_2$ : C, 65.97; H, 5.54.

Reaction of 10 and 11 with KOtBu

1  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR data see tab. 1 and 2) General procedure.

To a soln of 0.10 g of 10 resp. of 11 in 5 ml of THF a soln of 0.10 g of KOtBu in 5 ml of THF was added rapidly at 0 °C under  $\text{N}_2$ . After 1 hr at

0 °C 50 ml of an ice-cold 5%  $\text{NH}_4\text{Cl}$  soln were added. The mixture was extracted with ether. After evaporation the residue was chromatographed (PE/E 3:1).

Reaction of 10. - Besides 35 mg of recovered starting material (3. fraction) it was isolated:

1-t-Butoxy-c-2-(2-hydroxyethyl)-c-3-phenyl-r-1-cyclopropanecarboxylic acid lactone (21),

30 mg (40%), 2. fraction, oily. - IR:  $1725\text{ cm}^{-1}$  (CO). - MS: m/e = 260 ( $\text{M}^+$ , 0.5%), 204 (M -  $\text{C}_4\text{H}_8$ , 18), 187 (M - OtBu, 10), 159 (18), 131 (28), 105 (28), 57 (100). - Found: C, 73.64; H, 7.72; calcd for  $\text{C}_{16}\text{H}_{20}\text{O}_3$ : C, 73.82; H, 7.74.

t-3-t-Butoxy-c-2-(2-hydroxyethyl)-c-3-phenyl-r-1-cyclopropanecarboxylic acid lactone (22),

17 mg (23%), 1. fraction, oily. - IR:  $1710\text{ cm}^{-1}$  (CO). - MS: m/e = 260 ( $\text{M}^+$ , 0.5%), 204 (50), 187 (15), 159 (100). Found: C, 73.69; H, 7.77.

Reaction of 11. - Besides 15 mg of recovered starting material (3. fraction) and 22 mg of an unseparable mixture of at least three compounds ( $^1\text{H}$ -NMR) it was isolated:

t-3-t-Butoxy-c-2-(2-hydroxypropyl)-c-3-phenyl-r-1-cyclopropanecarboxylic acid lactone (23)

53 mg (54%), 1. fraction, oily. - IR:  $1710\text{ cm}^{-1}$  (CO). - MS: m/e = 274 ( $\text{M}^+$ , 2%), 218 (M -  $\text{C}_4\text{H}_8$ , 100), 217 (70), 201 (20), 172 (50), 159 (95). - Found: C, 74.29; H 7.97; calcd for  $\text{C}_{17}\text{H}_{22}\text{O}_3$ : C 74.42; H, 8.08.

Reduction of lactones 21 and 23 ( $^1\text{H}$ -NMR see tab. 1). - General procedure.

To a stirred soln of 0.10 g of  $\text{LiAlH}_4$  in 10 ml of ether was added dropwise a soln of 0.1 mmol of 21 resp. 23 in 5 ml of ether at 0 °C. Stirring was continued at 0 °C for 1 hr and then worked up as usual with ice/dil.  $\text{H}_2\text{SO}_4$ .

1-t-Butoxy-c-2-(2-hydroxyethyl)-c-3-phenyl-r-1-cyclopropanemethanol (24).

From 21, 98% yield, m.p. 104 °C. -

Found: C, 72.55; H, 9.07; calcd for  $C_{16}H_{24}O_3$ : C, 72.69; H, 9.15.

t-3-t-Butoxy-c-2-(2-hydroxypropyl)-c-3-phenyl-r-1-cyclopropanemethanol (25)

From 23, 94% yield, oily. - Found: C, 73.18; H, 9.31; calcd for  $C_{17}H_{26}O_3$ : C, 73.34; H, 9.41.

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NOTE

This paper is dedicated to Professor Dr. Dieter Klamann on the occasion of his 60th birthday.