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43. d^5-Reactions of Doubly Deprotonated γ,δ-Unsaturated Carbonyl Derivatives with Electrophiles. A Novel Approach to the Synthesis of Tetrahydrofuran and Tetrahydropyran Derivatives[1])[2])

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(23. IX. 81)

Summary

The dienone-dianion derivatives **1** react with all types of electrophiles tested (alkyl halide, silyl chloride, ester, ketone, aldehyde, epoxide) to give β,γ-unsaturated carbonyl compounds of type **A** (see *Formulae* **2–6, 13, 14** and *Tables 1–5*). The α- and β-hydroxyalkylation products obtained from **1a–1d** can be converted to tetrahydrofuran and tetrahydropyran derivatives **7** and **16**, respectively *(Tables 1* and *2)*, those from the sulfur analogues **1e** and **1f** to ketene thioacetals **9** and to dienone derivatives **10** and **12**. The *t*-butyl and α-hydroxy-ketones are cleaved to give nitriles, amides, carboxylic acids and esters (*Formulae* **16–25**). The reagents **1** allow to synthesize products with distant functional groups in one step (*cf.* 1,8-diketones **14** and *Formulae* **26–30**); they correspond to the d^5-synthons **31–33**; in *Table 6*, they are compared with other d^5-reagents.

1. Introduction. – In connection with our work on reactivity umpolung with dianions[8]) we discovered, that the novel reagents of type **1** can be generated by double deprotonation in the α- and β-position of γ,δ-unsaturated carbonyl compounds and their dithio-analogues. In a preceding paper [1], we described the preparation of the starting materials, the optimization of the two successive deprotonations leading to

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[8]) See references on redox umpolung in our review article [2].

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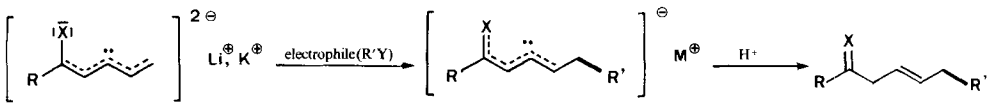
1 (potassium hydride, *sec*-butyllithium/TMEDA), and the reactions with benzophenone. It was found that the sole products resulting from C,C-bond formation with this electrophile have the general structure **A** [R′ = $C(OH)(C_6H_5)_2$][9]). It is the purpose of the present paper to demonstrate, that **1** acts as a d^5-reagent[10]) with all common electrophiles, and that the products of type **A** are amenable to a variety of transformations leading to synthetically useful intermediates.

Scheme 1[9])



1[11])	X	R
a	O	CH_3
b	O	$C(CH_3)_3$
c	O	$C(O^-)(CH_3)_2$
d	O	C_6H_5
e	S	SCH_3
f	S	$SCH(CH_3)_2$

A

2. Reactions of dienone-dianion derivatives *1* with electrophiles leading to products of type *2*. – 2.1. *Alkylation, acylation and silylation.* The trianion of **1c** (with R = $C(O^-)(CH_3)_2$) and the dianion derivative **1d** are alkylated with 1-bromo-3-chloropropane, methyl iodide, and butyl chloride to give the chain-elongated products **2** in yields between 60 and 70%; **2ca** is obtained after reaction at –78 to 0°, **2da** is formed with spontaneous discharge of the deep red-violet color of **1d** by methyl iodide at –78°, while heating the reaction mixture to room temperature is necessary to yield **2db** with the butyl chloride. No alkylation products other than **2** could be detected. Likewise, chlorosilane furnishes the *C(ω)*-silylated compounds **3** exclusively. The best way of preparing **3ba** is to add excess chlorotrimethylsilane to the reagent **1b**, forming the *C*- and *O*-silylated compound **4**, which gives the desired product on dissolution in methanol.

Acylation of **1** does not appear to be a favorable process: methyl isobutyrate converts **1b** to the 1,6-diketone[12]) **5** in 23% yield only; besides 2% of the diadduct, a 6-hydroxy-1,11-diketone, the product of a kinetic protonation[1]) of **1b**, the *β,γ*-unsaturated ketone[1]), is isolated. Attempts to acylate **1** with the non-enolisable methyl benzoate were also unsatisfactory.

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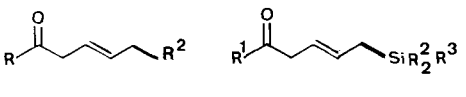
9) Newly formed bonds are indicated by heavy lines throughout this paper.

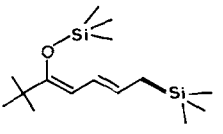
10) For the a,d-nomenclature of synthetic methodology see [2].

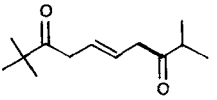
11) The letters **a–f** are also used as *first* letters in all product numbers to indicate the origin of the products from **1a–f**, respectively. For the meaning of the second letters to design derivatives of type **A** in the fortcoming text see *Schemes 2* and *3*, and *Table 1*.

12) For the preparation of such 1,6-diketones see [3].

Scheme 2[9][11])







2ca $R = C(OH)(CH_3)_2$, $R^2 = (CH_2)_3Cl$
2cb $R = C(OH)(CH_3)_2$, $R^2 = C_4H_9$
2cc $R = C(OH)(CH_3)_2$, $R^2 = CH_2C_6H_5$
2da $R = C_6H_5$, $R^2 = CH_3$
2db $R = C_6H_5$, $R^2 = C_4H_9$

3ba $R^1 = t\text{-}C_4H_9$, $R^2 = R^3 = CH_3$
3bb $R^1 = R^3 = t\text{-}C_4H_9$, $R^2 = CH_3$

4

5

2.2. *Reactions of* **1** *with aldehydes, ketones, and enones and cyclizations of the hydroxyalkylated products* **6** *to tetrahydrofurane derivatives* **7**. The additions of reagents **1** to aldehydes and ketones furnish after protonation nonconjugated, unsaturated 6-hydroxycarbonyl derivatives **6a–d**. All the examples are listed in *Table 1*. As can be seen, the yields, which are not optimized, are generally good, but only moderate with readily enolisable components.

The additions are totally ambidoselective[13]) with **1a–d** (X = O): in the numerous chromatographic product purifications and isolations, which we carried out, we have never detected a compound which resulted from C,C-bond formation at any other C-atom of **1** but the terminal one. Besides starting materials, we found only double-bond shifted isomers of the enone, from which **1** had been generated. In the reactions of **1** with benzophenone [1], up to 10% of the dimers of the precursor of **1** were present as impurities. The separation of the analytically pure substances **6** in the yields stated in *Table 1* is accomplished by a simple chromatography over silica gel. In the reactions of the phenyl-substituted **1d**, we noticed an increase of yields when a hexamethylphosphoramide (HMPA) solution of the carbonyl compound was added, rather than the usual tetrahydrofuran (THF) solution. When treated with base (sodium methoxide in methanol/THF) the alcohols **6a–d** (X = O) cyclize quantitatively to the tetrahydrofuran derivatives **7**, which are obtained in analytically pure form, after reaction times of 0.5–6 hours (see *Table 1*) at ambient temperatures, by a filtration through a short silica gel column or by short path distillation in the yields also included in *Table 1*. Aldehyde and ketone adducts of type **6** with $R^2 \neq R^3$ lead to mixtures of *cis*- and *trans*-diastereomers **7** as evident from capillary GC. and from the ^1H-, ^{13}C-NMR. spectra. A preparative separation and configurational assignment of the diastereomers were not possible. Since the ratios did not change on prolonged base treatment (*cf.* the tetrahydropyrans, *Section 2.3*), we do not know whether they are kinetic or thermodynamic ratios[14]).

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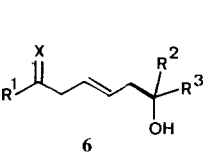
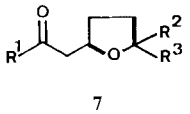
[13]) A structurally defined selectivity nomenclature is proposed in [2].

[14]) In the case of tetrahydrofuranylacetates, prolonged treatment with base establishes the thermodynamic equilibrium in which the *cis*-isomers prevail [4].

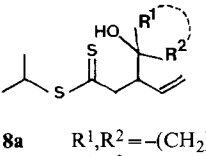
Scheme 3[9][11])



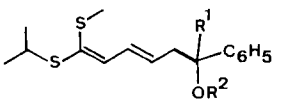
6



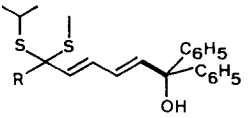
7



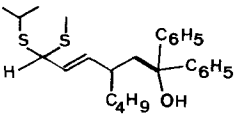
8a $R^1,R^2=-(CH_2)_4-$
b $R^1,R^2=-(CH_2)_5-$



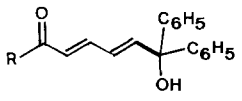
9a $R^1=H$, $R^2=CH_3CO$
b $R^1=C_6H_5$, $R^2=H$



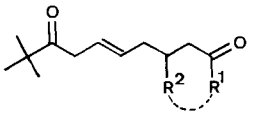
10a R = H
b $R=CH_3$
c $R=C_2H_5$



11



12a $R=CH_3$
b $R=C_2H_5$



13a $R^1=CH_3$, $R^2=H$
b $R^1,R^2=-(CH_2)_2-$
c $R^1,R^2=-(CH_2)_3-$
d $R^1,R^2=-(CH_2)_4-$

In view of the great tendency of sulfur-containing allylic and pentadienylic anion derivatives [5] to steer reactivity to the C-atom α to sulfur[13]) [7], it is not surprising that the reagents **1e** and **1f** (X = S), are not as ambidoselective[13]) as their analogues **1a–d** (where X = O): besides the d^5-products **6f**, the d^3-products of type **8** are formed in 2–10% yield (see *Table 1*). They are easily separated during chromatographic isolation of **6f**; only the adduct **8** to cyclopentanone was obtained in a pure state and was fully characterized. The alkoxide-thioenolates primarily formed from benzaldehyde and benzophenone and **1f** can not only be quenched with acid (→ **6fd** and **6fh**, respectively) but also with methyl iodide which leads to the unsaturated conjugated keten thioacetal derivatives **9** after aqueous workup[15]). This represents a novel synthetic approach to this versatile class of compounds [5] [7]. We have deprotonated **9b** with excess lithium diisopropylamide (LDA), and quenched the resulting alkoxide-pentadienyl-anion derivative with acid (→ **10a**), methyl iodide (→ **10b**) and ethyl iodide (→ **10c**). In contrast to the LDA, butyllithium does not react cleanly with **9b**, a (4:1)-mixture of **10a** and **11**, the result of an a^4-reaction[11]), is formed after aqueous workup. Alkylative hydrolyses [5] of the thioacetals **10b** and **10c** give the dienones **12a** and **12b**, respectively.

With the *t*-butyl-substituted reagent **1b**, we checked the possibility of achieving *Michael*-additions to enones such as methyl vinyl ketone (MVK), cyclopentenone, cyclohexenone and cycloheptenone. In total yields ranging from 25 to 45%, readily separated mixtures of the 1,2-adducts **6bg**, **6bh** and **6bi** (see *Table 1*) and of the

[15]) The *(E)*-configuration is assigned to **9** in analogy with our previous work [6].

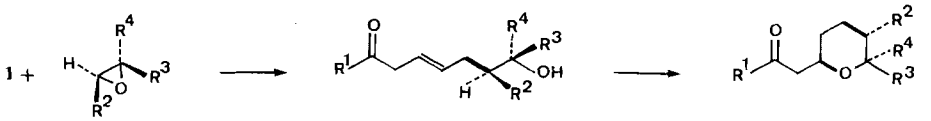
Table 1. *Products* **6** *from the reactions of the LiK-derivatives* **1** *with aldehydes and ketones, and tetrahydrofurans* **8** *obtained from the hydroxyketones* **6**. (For physical data of **6** and **7** see the *Experimental Part*. The benzophenone adducts **6ad, 6bi, 6df, 6ec, 6fh** are described in full detail in the preceding paper[1]). The yields refer to chromatographed, analytically and spectroscopically pure products. The yields of products from **1a** are calculated from the amount of electrophile employed[1]). Yields given in parentheses (+x) for the thiones **6f** refer to the side products of type **8**. The crude tetrahydrofurans **7** show spectra identical with those of analytically pure samples. Yield ranges are given where optimizations have been carried out, all other experiments have been done only once).

Starting materials	R^1, R^2 and R^3 in **6** and **7**				**6** (from **1**)		**7** (from **6**)			
	X in **6**	R^1	R^2	R^3		Yield [%]		Reaction time [h]	Yield [%]	Diaster. ratio
1a+										
Benzaldehyde	O	CH_3	C_6H_5	H	**6aa**	50–57	**7aa**	4	63	53:47
Cyclohexanone	O	CH_3	$-(CH_2)_5-$		**6ab**	25				
Acetophenone	O	CH_3	C_6H_5	CH_3	**6ac**	35	**7ac**	4	65	62:38
Benzophenone	O	CH_3	C_6H_5	C_6H_5	**6ad**	72	**7ad**	1	84	
1b+										
Propanal	O	t-C_4H_9	C_2H_5	H	**6ba**	40	**7ba**	1.5	62	56:44
2-Methylpropanal	O	t-C_4H_9	i-C_3H_7	H	**6bb**	48–65	**7bb**	1.5	78	62:38
Benzaldehyde	O	t-C_4H_9	C_6H_5	H	**6bc**	63–69	**7bc**	0.5	82	58:42
Acetone	O	t-C_4H_9	CH_3	CH_3	**6bd**	23				
2,2-Dimethyl-6-hepten-3-one	O	t-C_4H_9	t-C_4H_9	C_4H_7	**6be**	23				
Cyclohexanone	O	t-C_4H_9	$-(CH_2)_5-$		**6bf**	38	**7bf**	1	75	
Methyl vinyl ketone	O	t-C_4H_9	$CH=CH_2$	CH_3	**6bg**	+ *Michael*-				
2-Cyclohexenone	O	t-C_4H_9	$-CH=CH-(CH_2)_3-$		**6bh**	-adduct,				
2-Cycloheptenone	O	t-C_4H_9	$-CH=CH-(CH_2)_4-$		**6bi**	see text				
Benzophenone	O	t-C_4H_9	C_6H_5	C_6H_5	**6bj**	60–80	**7bj**	1	82	
1c+										
Benzophenone	O	$C(CH_3)_2$ OH	C_6H_5	C_6H_5	**6ca**	70				
1d+										
Propanal	O	C_6H_5	C_2H_5	H	**6da**	35	**7da**	3	68	50:50
2-Methylpropanal	O	C_6H_5	i-C_3H_7	H	**6db**	35	**7db**	2	72	54:46
Benzaldehyde	O	C_6H_5	C_6H_5	H	**6dc**	53	**7dc**	6	94	61:39
Cyclohexanone	O	C_6H_5	$-(CH_2)_5-$		**6dd**	25	**7dd**	1	85	
1-Phenyl-4-penten-1-one	O	C_6H_5	C_6H_5	C_4H_7	**6de**	48	**7de**	4	65	62:38
Benzophenone	O	C_6H_5	C_6H_5	C_6H_5	**6df**	40–65	**7df**	5	86	
1e+										
Benzaldehyde	S	CH_3S	C_6H_5	H	**6ea**	43				
Cyclohexanone	S	CH_3S	$-(CH_2)_5-$		**6eb**	38				
Benzophenone	S	CH_3S	C_6H_5	C_6H_5	**6ec**	47–71				
1f+										
Propanal	S	i-C_3H_7S	C_2H_5	H	**6fa**	56(+2)				
2-Methylpropanal	S	i-C_3H_7S	i-C_3H_7	H	**6fb**	49(+2)				
2,2-Dimethylpropanal	S	i-C_3H_7S	t-C_4H_9	H	**6fc**	60(+2)				
Benzaldehyde	S	i-C_3H_7S	C_6H_5	H	**6fd**	61–73(+6)				
Acetone	S	i-C_3H_7S	CH_3	CH_3	**6fe**	39(+3)				
Cyclopentanone	S	i-C_3H_7S	$-(CH_2)_4-$		**6ff**	44(+11)				
Cyclohexanone	S	i-C_3H_7S	$-(CH_2)_5-$		**6fg**	55(+4)				
Benzophenone	S	i-C_3H_7S	C_6H_5	C_6H_5	**6fh**	84(+0)				

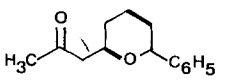
1,4-adducts **13** were obtained. Cyclopentenone gave only *Michael*-product **13b**; with cyclohexenone, the amount of conjugate addition decreased from *ca.* 3:2 to 4:3 when HMPA was added to the THF solvent. Thus, an a^3-d^5-process[11]) with formation of 1,8-dicarbonyl compounds of type **13** has been realized, albeit so far with low yields.

2.3. *Ring-opening of epoxides by the reagents* **1** *and ring-closure of the products* **14** *to tetrahydropyran derivatives* **15**. Epoxides are especially attractive electrophiles for several reasons: *i*) they are a^2-reagents and thus provide an umpolung of enolate d^2-reactivity[11]); *ii*) with many nucleophiles, they react regioselectively at the less substituted C-atom (S_N2-type ring-opening); *iii*) they are readily available in diastereomerically pure forms from the corresponding *(E)*- and *(Z)*-olefins; *iv*) since ring-opening normally takes place with inversion, configurational purity is retained in the products (diastereoselectivity); *v*) many epoxides have become accesible in enantiomerically pure form [8], which also allows the synthesis of chiral products through this versatile class of compounds. Disadvantages can be *i*) the rather slow reactions with many nucleophiles, organolithium compounds generally require temperatures above –10°C, and *ii*) the pinacole rearrangements occurring with highly reactive organolithium and even more so with organomagnesium compounds (*Lewis*-acid character). We were pleased to find that addition of epoxides to well stirred solutions of **1a–d** (X = O), at –78°C and warming to room temperature gives the 7-hydroxy-ketones of type **14** after aqueous workup (see *Table 2*). Opti-

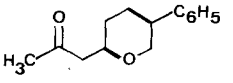
Scheme 4[9])[11])



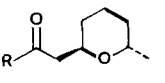
14 **15**



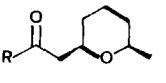
15ab



15ac

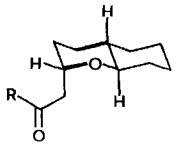


trans **15ba**

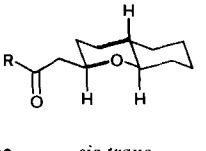


cis (more stable) **15ca**

(R, see *Table 2*)



trans-trans **15bc**



cis-trans (more stable) **15cc**

(R, see *Table 2*)

mized yields of up to 70% were reached even if a substituted C-atom (2-butene and cyclohexene epoxide) had to be attacked by the reagents **1**. Sampling during the warm-up period proved that the reactions do not ensue below –20° C. Methyloxirane and 2,2-dimethyloxirane but not phenyloxirane are opened regioselectively, 1,2-epoxycyclohexane diastereoselectively (with inversion) (see *Table 2* and *Formulae* **16** in *Scheme 4*). The chromatographic product isolation furnished only the precursor ketone **1** and its double-bond-shifted isomers as easily separated impurities. With the dithio-analogues **1e** and **1f**, the temperatures necessary for reaction with epoxides cannot be attained; the reagents start decomposing above –50° C.

The hydroxy-enones **14** are cyclized by base to the tetrahydropyran derivatives (THP) **15** under the same conditions which convert the carbonyl adducts **6** to THF-derivatives **7** *(Section 2.2.)*. Again, the crude products are obtained quantitatively, yields of analytically pure samples are given in *Table 2*.

Table 2. *Hydroxy-enones* **14** *and tetrahydropyrans* **15** *from reactions of* **1** *with epoxides* (All yields refer to chromatographed, analytically pure products. Yield ranges are given in those cases where reactions were optimized)

Starting materials	R^1,R^2,R^3,R^4 in **14** and **15**				**14** (from **1**)		**15** (from **14**)			
	R^1	R^2	R^3	R^4		Yield [%]		Reaction time [h]	Yield [%]	*(cis/trans)*-Ratio
1a +										
2,2-Dimethyloxirane	CH_3	H	CH_3	CH_3	**14aa**		**15aa**		29	
2-Phenyloxirane	CH_3	H	C_6H_5	H	**14ab**		**15ab**		15	*cis* (?)
	CH_3	C_6H_5	H	H	**14ac**		**15ac**		23	*trans* (?)
1b +										
2-methyloxirane	*t*-C_4H_9	H	CH_3	H	**14ba**	43–50	**15ba**	1.5	82	59:41
								96		100:0
2,2-Dimethyloxirane	*t*-C_4H_9	H	CH_3	CH_3	**14bb**	53	**15bb**	2	77	
1,2-Epoxycyclohexane	*t*-C_4H_9	$-(CH_2)_4-$		H	**14bc**	48	**15bc**	3	82	74:26
								48		90:10
								70		100:0
1c +										
2-Methyloxirane	$C(OH)(CH_3)_2$	H	CH_3	H	**14ca**	56–65	**15ca**	2	>90	100:0
trans-2,3-Dimethyloxirane	$C(OH)(CH_3)_2$	CH_3	H	CH_3	**14cb**	59–60				
1,2-Epoxycyclohexane	$C(OH)(CH_3)_2$	$-(CH_2)_4-$		H	**14cc**	52–70	**15cc**	2	>90	100:0
1d +										
2,2-Dimethyloxirane	C_6H_5	H	CH_3	CH_3	**14da**	32	**15da**	1	71	

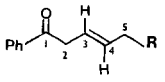
The two constitutional isomers derived from phenyloxirane cyclize to the THP-derivatives **15ab** and **15ac** (both diastereomerically pure). Short reaction times lead to diastereomeric mixtures of the methyloxirane and 1,2-epoxycyclohexane-derived tetrahydropyranes **15ba** and **15bc** which are epimerized – due to the reversibility of the ring-closure 6-*exo*-dig-process[16]) – to the thermodynamically more stable *cis*-isomers after longer periods of time; on the other hand, the analogous products from the trianion derivative **1c**, the hydroxyketone-substituted tetrahydropyrane derivatives **15ca** and **15cc** are obtained as single diastereomers after 2 hours reaction time

16) Rules and nomenclature for ring closures, see [9].

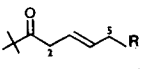
with base (see *Table 2* and *Formulae* **15** in *Scheme 4*). Our configurational assignments rest almost (see **22**, *Section 4*) entirely upon the expected greater stability of equatorial 2-alkyltetrahydropyrane derivatives.

3. Assignment of *(E)*-configuration to the products of type *A*. – In a preliminary communication of the results obtained with the phenyl derivative **1d**[2]) [10] we had *erroneously* assigned the *(Z)*-configuration to all products from non-aromatic electrophiles on the basis of the poorly analyzed multiplets of the vinylic protons in the ^{1}H-NMR. spectra. We are now convinced that – with the exception of the products derived from the triply metallated reagent **1c** – the compounds of type **A** have the *(E)*-configuration on the following grounds (see also *Exper. Part*): In their IR. spectra, the 960–990 cm^{-1}-bands characteristic of *(E)*-disubstituted double bonds are present. ^{1}H-NMR. decoupling experiments with the products from the phenyl derivative **1d** show typical 14.0–16.0 Hz *(E)*-coupling constants in all cases (see *Table 3*). On the other hand, 360-MHz-^{1}H-NMR. analysis of *t*-butyl ketones **6be, 6bi** and **14ba** with decoupling furnished the borderline value of 11.0 Hz in all three cases. We have therefore applied the increment method [11] to analyze the ^{13}C-NMR. spectra of the β,γ-unsaturated ketones **6be, 6bi** and **14ba**: the chemical shifts calculated for the allylic α-carbonyl-C-atoms with *(E)*-configuration agree satisfactorily with the experimental values. The results are summarized in *Table 4*.

Table 3. *The coupling constants and chemical shifts obtained from decoupling experiments*



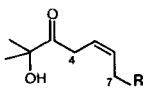
Product	Decoupled protons	Coupling constant (Hz)	Chemical shifts of the olefinic protons (δ,ppm)	
			H–C(3)	H–C(4)
2da	$H_2C(2)$	16.0	5.65	–
	$H_2C(5)$	16.0	–	5.52
2db	$H_2C(2)$	16.0	5.68	–
	$H_2C(5)$	16.0	–	5.58
6da	$H_2C(2)$	16.5	5.8	–
	$H_2C(5)$	16.0	–	5.56
6db	$H_2C(2)$	15.0	5.7	–
	$H_2C(5)$	15.0	–	5.56
6dc	$H_2C(2)$	16.5	5.79	–
	$H_2C(5)$	16.0	–	5.64
6dd	$H_2C(2)$	14.0	5.65	–
	$H_2C(5)$	14.5	–	5.52
6de	$H_2C(2)$	16.0	5.7	–
	$H_2C(5)$	16.0	–	5.33
6df	$H_2C(2)$	16.0	5.85	–
	$H_2C(5)$	16.0	–	5.64
14da	$H_2C(2)$	15.5	5.8	–
	$H_2C(5)$	16.0	–	5.58

Table 4. *^{13}C-NMR. ($CDCl_3$) – Chemical shifts of C(2)* 

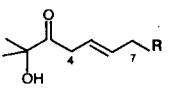
Product	Chemical shifts calculated [11]		Chemical shifts observed
	Z	*E*	
6bi	32.9	38.9	40.19
6be	32.9	38.9	37.58
14ba	32.9	38.9	38.61

In contrast, careful chromatographic separation or enrichment and ^{13}C-NMR. analysis of the d^5-products **2cb, 2cc, 6ca** and **14ca** obtained from the lithium-dipotassium derivative **1c** and *t*-butyl bromide, benzyl bromide, benzophenone, and 2-methyloxirane, respectively, showed that these compounds are mixtures of *(E)*- and *(Z)*-diastereomers. As is evident from *Table 5*, the ^{13}C-NMR. chemical shifts of the allylic C-atoms of the major isomers are all smaller by 5–6 ppm than the corresponding shifts of the minor isomers. In this case, the increment method fails to reproduce the measured values, compare *Tables 4* and *5*, but we think that it is allowed to assign the *(Z)*-configuration to the diastereomer with the relative high-field resonances of the allylic C-atoms (see *Table 5*).

Table 5. *^{13}C-NMR. chemical shifts of the allylic C-atoms of products from* **1c** (The ratios of major to minor isomer were determined by ^{1}H-NMR.-integration (**6ca**) or approximately by comparison of peak intensities in ^{13}C-NMR.-spectra. We have tentatively assigned the *(Z)*-configuration to the major isomer which has resonances at *ca.* 6 ppm upfield from the minor isomer as predicted [11])



Z



E

Product		Isomer ratio	Chemical shift			
No.	R		Major isomer		Minor isomer	
			C(4)	C(7)	C(4)	C(7)
2cb	C_4H_9	4:1	34.49	27.64	39.61	32.71
2cc	$CH_2C_6H_5$	4:1	34.43	31.98	39.38	38.15
6ca	$C(OH)(C_6H_5)_2$	6:1	34.60	40.04	39.49	45.35
14ca	$CH_2CH(OH)CH_3$	7:1	34.43	23.82	39.44	28.94

4. Conversion of α-(tetrahydro-2-furanyl)- and α-(tetrahydro-2-pyranyl)ketones *7* and *15*, respectively, to carboxylic acid derivatives. Synthesis of a *Civet* component. – Although the di- and trianion derivatives **1** and their reactions deserve interest of their own, the R-groups were chosen[1]) with the aim to cleave the (R–CO)-bond in the products obtained from **1**, *i. e.* eventually to prepare carboxylic acid derivatives and thus to have access essentially to all important functional groups through the reagents of type **1** (see discussion in *Section 5*). Since it is well established that tertiary alkyl and aryl groups have a larger migratory aptitude in sextett rearrange-

ments than primary alkyl groups, we first tried such reactions with products from the *t*-butyl- and the phenyl-substituted nucleophiles **1b** and **1d**. In order to avoid complications caused by the presence of a C,C-double bond[17]) under the *electrophilic* conditions of sextett rearrangements – highly electrophilic or *Lewis*-acidic reagents and intermediates are involved – we decided to use the THF- and THP-derivatives **7** and **15** as starting materials, first, utilizing the heterocyclic ring as a double-bond protecting group (see **22**→**25**, below). The *Baeyer-Villiger* [12] oxidation of both phenyl- and *t*-butyl ketones **7b** and **15b** was a big disappointment: only very low conversions could be achieved under a variety of conditions, even with the normally most effective trifluoroperacetic acid[18]). We therefore turned our attention to the *Beckmann* rearrangement [13]. The oximes of the *t*-butyl ketones **7bc, 7bj, 15ba** and **15bc** were readily prepared following a standard procedure [14]. Upon treatment of the oxime of **7bj** with PCl_5 in anhydrous diethyl ether (see *Scheme 5*) a separable mixture of the amide **17** (26%), the normal rearrangement product, and of the nitrile **18** (69%), the *Beckmann*-type II [13b] elimination product, was isolated. Hydrolysis with sodium hydroxide in glycol converted this mixture to the acid **16a**, which was esterified to its methyl ester **16b** (64% overall yield from the oxime). Similarly, a diastereomeric mixture **19** was prepared from the oxime of **7bc**. The THP-derivatives **15** led to the nitriles **20** (69% overall from the ketone) and **21a** (80%). The acid (±)-**22a** obtained from the nitrile **20** was identical with a sample which was recently isolated from the civet *(Viverra civetta)* and synthesized by a different route [15]. Because too small amounts of the natural product were available to even measure a rotation, it was neither possible to tell whether it was optically active nor which sense of chirality (absolute configuration) it had. We had also prepared the optically active acid **22a** from (–)-*(S)*-methyloxirane [16]. Comparison of the methyl ester **22b** by NMR.spectroscopy in the presence of chiral shift reagent proved the *(S,S)*-chirality of the natural product [17]. The results described demonstrate that the *Beckmann* rearrangement provides an efficient rout from the *t*-butyl ketones **7** and **15** to nitriles (2 steps) and to carboxylic acids (3 steps).

By far the best group R in **1** for eventual cleavages is, however, the 1-hydroxy-1-methylethyl group [18]: α-hydroxyketones are converted to carboxylic acids by glycol-cleaving reagents. The *cis*-tetrahydropyranylmethyl-(α′-hydroxy)-ketone **15ca** and the hexahydrochromanyl analogue **15cc** are for instance converted instantaneously to the acids **22a** and **21b**, respectively, when treated with periodate in aqueous THF. This one step reaction is also much milder than the processes involved in the *Baeyer-Villiger* sequence. It is even applicable to the open-chain products of **1c** with electrophiles: the unsaturated dihydroxyketones **14ca** and **14cc** are cleaved quantitatively to the corresponding acids **23** and **24**, respectively. In order to get back to non-cyclic compounds, the oxime route requires yet another step, as demonstrated by the preparation of the acids **25**. Treatment of the diphenyl-substi-

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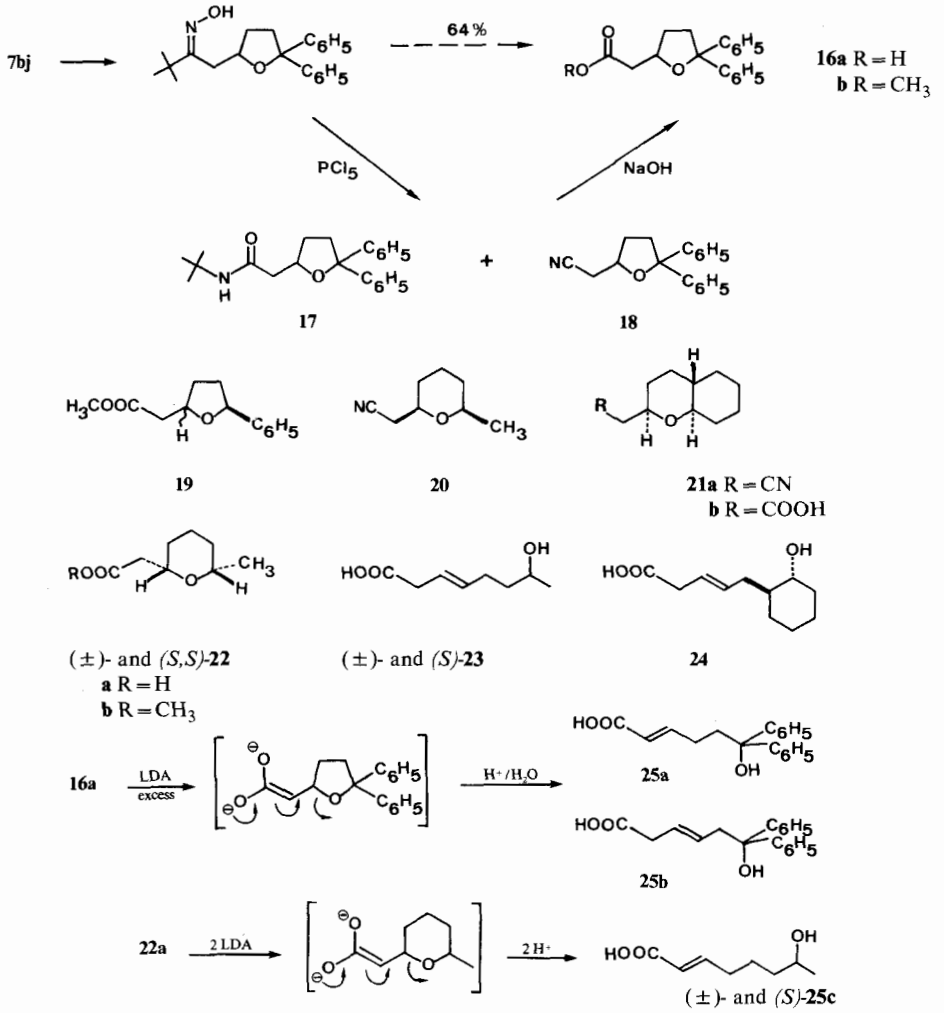
17) The oxime of the *O*-acetyl-**15ba** gave, for instance, a mixture of the desired nitrile and the saturated 5-chloro-6-cyano-1-methylhexyl acetate when treated with PCl_5 under the conditions of a *Beckmann* rearrangement.

18) The fact, that 90% H_2O_2-solution is no more commercially available in Europe, may at least partially have been responsible for our lack of success with this reaction.

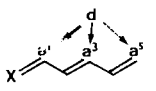
tuted THF-acetic acid **16a** with 2.0–2.2 mol-equiv. of lithium diisopropyl amide (LDA) leads to a mixture of the conjugated acid **25a** and of the non-conjugated isomer **25b**, while three mol-equiv. of the base and subsequent protonation furnish **25b** exclusively (probably through a trianion)[19]). In the same way **22a** is converted to the acid **25c**, the conjugated isomer of **23**. The use of the hydroxy acids **24** and **25c** which we also prepared in the enantiomerically pure *(S)*-forms for the synthesis of the antibiotic diolide pyrenophorin [16] [19] has been described in detail elsewhere [16].

Scheme 5



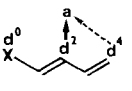
[19]) The doubly deprotonated oxime of the THF-ketone **7bj** also openes up to the oxime of the α,β-unsaturated-ε-hydroxy-ketone, while the ketone enolates of **7b, 7d, 15b** and **15d** do not appear to undergo cleavage of the cyclic ether (reversible cleavage obviously occurs in the *trans-cis*-equilibrations of **15b** (see *Section 2.3*)).

5. Discussion of the Results. – There is a great need for reagents in organic synthesis which exhibit *remote reactivity*. With few exceptions, *kinetically* controlled reactions of functional groups with conjugated double bonds occur in the neighbourhood of the functional groups[20]): a^1- *vs.* a^3- and a^5-reactivity[11]) of enones and dienones, d^2- *vs.* d^4-reactivity of dienolates, silyl dienol ethers and dienamines, d^1 *vs.* d^3- and d^5-reactivity of heterosubstituted allyl and pentadienyl anion derivatives, see **26–28**. Thermodynamic control, which is limited to reversible processes, on the other hand, leads to products of coupling at remote C-atoms. The most important result of the present study is the finding that switching to derivatives of dianions **29** (doubly LUMO-filled dienones) [2] not only provides a reactivity umpolung – our original goal – but also secures ω-reactivity with all electrophiles including «irreversible» ones (alkyl halides, epoxides). This is in agreement, *i*) with simple *Hückel*-calculations, according to which the largest coefficient of the highest occupied orbital ψ_4 in a 1-oxahexatriene-dianion is at the terminal C-atom which also bears the highest negative π-charge density of all five C-atoms [20] *ii*) with the resonance structure **30** having the largest charge separation, and *iii*) with the thermodynamically most stable product structure **31**. Although we have no information about the actual structure of the reagents of type **1**, their chemistry suggests that they may be described properly as a combination of a more stable – less reactive – enolate ion with a less stable – more reactive – allyl anion derivative (see for instance the acylation and silylation at C-atom). Their thermal stability (up to and above 0°C) and the smooth S_N2-type reactions with epoxides are compatible with this description of a soft allylic nucleophile; we would not expect such behaviour of a «hot», alkyllithium or -potassium reagent.



26

X = O, NR

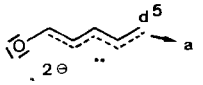


27

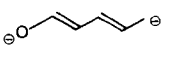
$X = O^-$, RO, RN^-, R_2N

28

X = Hal., OR, NR_2, RN(NO) SR, SOR, SO_2R



29



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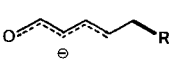


31

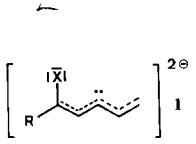
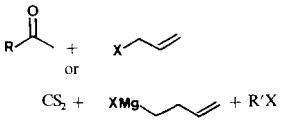
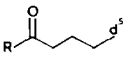
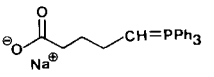
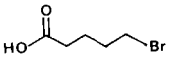
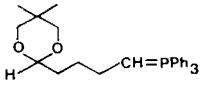
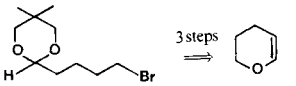
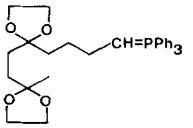
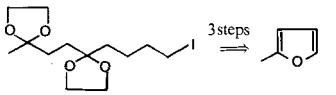
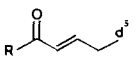
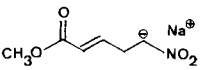
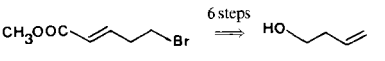
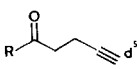
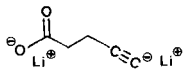
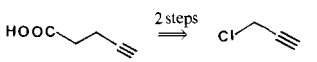
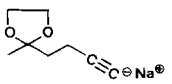
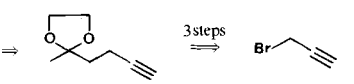
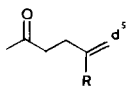
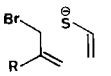
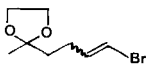
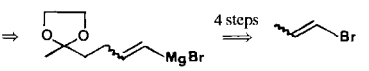
Even more difficult than to achieve ω-reactivity as such is the control of stereochemistry remote from functional groups of open-chain compounds. The reactions of the Li,K-derivatives **1a–1d** with epoxides offer a possibility to solve that problem efficiently; see the hydroxy-ketones **14**, the hydroxy-acids **23–25**, and the THP-derivatives **15** and **20–21**.

The general synthetic usefulness of the new reagents must be judged from several points of view. Except for special applications, the R-group in **1** should not

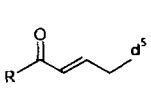
[20]) This is especially true of intermolecular reactions of open-chain derivatives.

contain CH-protons in α'-position to carbonyl (as does **1a**), should to some extent sterically protect the carbonyl C-atom [21] and should be readily cleaved off. Therefore, the 1-hydroxy-1-methylethyl derivative **1c** is the most promising one. We are presently investigating at which positions the system **1** can be substituted. In our

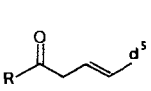
Table 6. *Synthon comparison of reagents* **1** *with other* d^5*reagents from the recent literature*

d^5-Synthon	d^5-Reagent	Precursors	Ref.
31–33			This work and preceding papers [1] [2] [10] [19]
			[24]
			[25]
			[26]
			[27]
			[28]
			[29]
			[30]
			[31]

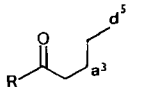
continuing efforts to apply the reagents **1** to natural product synthesis we find that the, admittedly, often moderate yields of products of type **A** *(Table 1, 2* and *Exper. Part)* can be increased by careful optimization. Even if this were not the case, the straightforward access to the structures described here renders the method attractive enough, see the synthons **32–34**; R can not only be the groups originally present in **1**, but also OH, OR and all other groups which can be introduced through the carboxylic acid function, RCO can be set equal to C≡N and by way of reductions to RCH(OH), CH_2OH, CH_2X and CH_2NH_2. Furthermore, the principle by which the THF- and THP-derivatives are constructed here (see **33**) constitutes an extension of the methodology [22] [23]. Other reagents corresponding to d^5-synthons are listed in *Table 6*. If the syntheses of the precursors, the functionality patterns in the products and the scopes and reactivities are included into consideration and comparison, it becomes evident that our approach may very well turn out to be the most versatile one.



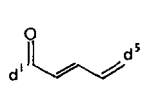
32a
(*cf.* **25**)



32b
(*cf.* **2, 3, 5, 6, 13, 14, 23, 24**)



33
(*cf.* **7, 15, 16, 22**)



34
(*cf.* **10, 12**)

We gratefully acknowledge financial support and technical assistance by the same institutions, companies and people whose names are given in [1].

Experimental Part

General remarks. Melting points are determined on a melting point apparatus *Büchi* 510 and are uncorrected. The boiling points reported are the bath temperatures during Kugelrohr or short path distillations. Spectral measurements were effected with *Perkin-Elmer* 297, 283 or 225 infrared grating spectrometer (IR.); *Varian T-60, A-60, CFT20, EM390, XL100, Jeol-Minimar 100* spectrometer (NMR.); *Varian MAT 111* GC-MS-System *Hitachi, Perkin-Elmer RMU-6M, Varian MAT 311* (MS.); *Perkin-Elmer 241* polarimeter (optical rotation). The chemical shifts are reported in δ (ppm) down field from TMS.

The solvent THF was first refluxed over KOH for several hours and distilled. It was again refluxed over $LiAlH_4$ under Ar-atmosphere and redistilled. THF required for reaction was taken out using a syringe. Ether was refluxed over KOH, distilled and stored over Na-wire. Pentane, benzene and CH_2Cl_2 were refluxed over P_2O_5 and distilled. TMEDA was first refluxed over KOH and distilled and again refluxed over $LiAlH_4$ and redistilled under reduced pressure (b.p. 72°/150 Torr). It was stored over molecular sieves in a bottle having a septum cap. HMPT was refluxed over CaH_2, distilled and stored over molecular sieves. Diisopropylamine was refluxed over $LiAlH_4$ and distilled into a bottle having a septum cap. Butyllithium (≈ 15% in hexane) used was supplied by *Metallgesellschaft.* TLC. was performed on *Polygram SIL G/UV 254* plastic sheets *(Macherey Nagel 4 CD)* and *Kieselgel f 254* plastic sheets *(Merck Darmstadt)* and was used to check the purity of the products.

1. Alkylation, silylation and acylation of the dianions of type *1*. – Experimental procedures for the generation of the dianions of type **1** have been described in the preceding paper [1].

1.1. *Preparation of the alkylation products* **2.** (E)-*10-Chloro-2-hydroxy-2-methyl-5-decen-3 one* (**2ca**). The trianion **1c** (2.84 g, 20 mmol) in THF (100 ml) was reacted with 1-bromo-3-chloropropane (4.02 g, 25.6 mmol) at –78°. It was stirred between –50 to –30° for 4 h and –30 to 0° for 11 h. The reaction mixture was cooled to –78° and acidified (pH 6) with 1.5N HCl in THF. On usual workup it furnished a crude product (3.1 g) which was purified by column chromotography over silica gel (80 g). On elution with pentane and ether/pentane 1:9 it gave **2ca** (2.28 g, 52%) as colourless oil, b.p. 110°/0.01 Torr, $n_D^{22} = 1.4773$. – IR. (film): 3450, 2970, 2926, 2855, 1700, 1455, 1360, 1310, 1186, 1165, 1055, 967. –

^{1}H-NMR. ($CDCl_3$): 1.4 (*s*, 6 H, 2 H_3C–C(2)); 1.7 (*m*, 4 H, 2 H–C(8,9)); 2.12 (*m*, 2 H, 2 H–C(7)); 3.35 (*m*, 2 H, 2 H–C(4)); 3.53 (*t*, *J*=6, 2 H, 2 H–C(10)); 3.6 (br. *s*, 1 H, OH); 5.63 (*m*, 2 H, CH=CH).

$C_{11}H_{19}O_2Cl$ (218.7) Calc. C 60.41 H 8.74 Cl 16.21% Found C 60.23 H 8.63 Cl 16.05%

2-Hydroxy-2-methyl-5-undecen-3-one (**2cb**). The trianion **1c** (5 mmol, in 20 ml THF) was reacted with 1-bromobutane (5 mmol) at –78°. The reaction mixture was allowed to warm to RT. for 15 h and quenched at –78° with 2.5 ml acetic acid. Usual workup and chromatography over silica gel yielded **2cb** (0.54 g, 55%, mixture of two isomers) as a colorless oil. – IR. (film): 3460 br., 3020, 2956, 2927, 2856, 1709, 1456, 1361, 1164, 1067, 972. – ^{1}H-NMR. (CCl_4): 0.75–1.05 (*m*, 3 H, 3 H–C(10)); 1.1–1.55 (*m*, 6 H, 2 H–C(8,9,10)); 1.32 (*s*, 6 H, 2 H_3C–C(2)); 1.8–2.2 (*m*, 2 H, 2 H–C(4)); 3.28 (*d*, *J*=4.5, 2 H, 2 H–C(4)); 3.5 (br. *s*, 1 H, OH); 5.35–5.75 (*m*, 2 H, CH=CH). – ^{13}C-NMR ($CDCl_3$): major isomer: 26.55 (C(1)); 76.71 (C(2)); 212.68 (C(3)); 34.49 (C(4)); 120.76, 133.66 (C(5) and C(6)); 27.64 (C(7)); 29.05 (C(8)); 31.55 (C(9)); 22.58 (C(10); 14.03 (C(11)); minor isomer: 39.61 (C(4)); 121.64, 135.18 (C(5) und C(6)); 32.71 (C(7)). – MS.: 140 (6), 112 (7), 98 (6), 96 (9), 69 (11), 59 (100), 55 (19), 43 (17), 41 (24).

2-Hydroxy-2-methyl-8-phenyl-5-octen-3-one (**2cc**). The trianion **1c** (5 mmol, in 20 ml THF) was reacted with benzyl bromide (0.87 g, 5.1 mmol) at –78°. After 30 min at –78° the reaction mixture was quenched with 2.5 ml acetic acid. Usual workup and chromatography over silica gel yielded **2cc** (0.49 g, 42%, mixture of two isomers) as a viscous oil. – ^{1}H-NMR. (CCl_4): 1.25 (*s*, 6 H, 2 H_3C–C(2)); 2.16–2.5 (*m*, 2 H, 2 H–C(7)); 2.5–2.8 (*m*, 2 H, $CH_2C_6H_5$); 3.12 (br. *d*, *J*=4.5, 2 H, 2 H–C(4)); 3.4 (br. *s*, 1 H, OH); 5.35–5.8 (*m*, 2 H, HC=CH); 7.0–7.35 (*m*, 5 H, arom. H). – ^{13}C-NMR. ($CDCl_3$): major isomer: 26.47 (C(1)); 76.65 (C(2)); 212.75 (C(3)); 34.43 (C(4)); 31.98 (C(7)); 27.21 (C(8)); minor isomer: 39.38 (C(4)); 38.15 (C(7)).

As a side product, 2,13-dihydroxy-2,13-dimethyl-5,9-tetradecadien-3,12-dione (43%) was obtained. – ^{1}H-NMR. (CCl_4): 1.3 (*s*, 12 H, 4 CH_3); 2.0–2.2 (*m*, 4 H, 4 CH–C=C); 3.15–3.4 (*m*, 4 H, 2 CH_2CO); 3.5 (br. *s*, 2 H, 2 (OH)); 5.4–5.7 (*m*, 4 H, 2 HC=CH).

(E)-*1-Phenyl-3-hexen-1-one* (**2da**). The dianion (**1d**, 5 mmol) in THF (15 ml) was treated with methyl iodide (0.35 ml, 5.5 mmol) at –78° and stirred at –78° for 2 h. Usual workup gave a crude product (0.8 g, 70% product determined by spectroscopic methods). After gas chromatography (*OV 17*, 120°) it furnished **2da**, n_D^{22}=1.5362. – IR. (film): 3030, 3010, 2968, 2960, 2810, 1685, 1620, 1600, 1580, 1445, 1260, 1200, 1180, 1070, 965 (*(E)*-(CH=CH)), 750, 690. – ^{1}H-NMR. (CCl_4): 1.0 (*t*, 3 H, *J*=6.5, 3 H–C(6)); 2.1 (*m*, 2 H, 2 H–C(5)); 3.14 (*m*, 2 H, 2 H–C(2)); 5.55–5.75 (*m*, *J*=15, 2 H, CH=CH); 7.5 and 7.9 (*m*, 5 H, aromat. H).

$C_{12}H_{14}O$ (174.2) Calc. C 82.75 H 8.04 Found C 82.77 H 7.95

(E)-*1-Phenyl-3-nonen-1-one* (**2db**). The solution of the dianion (**1d**, 10 mmol) in THF was treated with butyl chloride (0.925 g, 10 mmol) at –40° and stirred overnight (–40° to RT.). On usual workup 1.68 g of the crude product was obtained (59% determined by spectroscopic methods). After gas chromatography (*OV 17*, 130°) it gave **2db**, $n_D^{21.5}$=1.5288. – IR. (film): 1680, 1620, 1595, 1580, 1445, 1200, 965 (trans-CH=CH), 750, 680. – ^{1}H-NMR. (CCl_4): 0.7–1.3 (*m*, 9 H, 2 H–C(6), 2 H–C(7), 2 H–C(8), 3 H–C(9)); 1.95 (*m*, 2 H, 2 H–C(5)); 3.6 (*m*, 2 H, 2 H–C(2)); 5.6 (*m*, *J* (trans)=16, 2 H, CH=CH); 7.3 and 7.95 (*m*, 5 H, aromat. H).

$C_{15}H_{20}O$ (216.3) Calc. C 83.33 H 9.25% Found C 83.49 H 9.48%

1.2. *Preparation of the silylation products* **3** *and* **4**. – *2,2-Dimethyl-7-(trimethylsilyl)-5-hepten-3-one* (**3ba**) *and 6,6-Dimethyl-1-(trimethylsilyl)-5-(trimethylsilyloxy)-2,4-heptadiene* (**4**). The solution of the dianion **1b** (10 mmol) in THfF was treated with trimethylchlorosilane (5.04 ml, 40 mmol) at –78°. After stirring at –78° for 40 min, the reaction mixture was poured into $NaHCO_3$-solution (5%) and extracted with pentane (2×50 ml). The combined organic phase was washed twice with $NaHCO_3$-solution (5%) and twice with cold water. After drying ($MgSO_4$), the solvent was removed under reduced pressure to give a crude product (2.54 g). It was purified by passing over silica gel (100 g) using ether/pentane 2:98, to furnish **4** (2.05 g, 72%). After distillation it gave the pure product **4** (1.8 g, 63%) as colorless oil, b.p. 80°/0.005 Torr., n_D^{21}=1.4687. – IR. (film): 3040, 3015, 2960, 2800, 1645, 1600, 1480, 1400, 1390, 1360, 1315, 1255, 1220, 1175, 1130, 1075, 960, 945, 850, 780, 750, 730, 690, 670. – ^{1}H-NMR. (CCl_4): 0.0 (*s*, 9 H, 3 H_3C–Si–C); 0.23 (*s*, 9 H, 3 H_3C–Si–O); 1.06 (*s*, 9 H, 3 H_3C–C(5)); 2.53 (*d*, *J*=9, 2 H, 2 H–C(1)); 5.06–5.43 (*m*, 2 H, olefin. H); 5.93 (*d*×*d*, *J*=9 and 11, 1 H, olefin. H).

$C_{15}H_{32}OSi_2$ (284.6) Calc. C 63.31 H 11.33% Found C 63.44 H11.37%

Hydrolysis of **4** *to* **3ba**. The crude product **4** (3.2 g) was dissolved in methanol/water 80:20 and stirred overnight at RT. The reaction mixture was poured into a mixture of water and pentane and extracted three times with pentane. The combined organic phase was washed with water and sat. NaCl-solution. After drying ($MgSO_4$) the solvent was removed under reduced pressure to give the crude product (1.87 g). It was purified by passing over silica gel (60 g) with ether/pentane 2:98 to furnish **3ba** (1.04 g, 49%) as colorless oil, b.p. 80°/0.75 Torr, $n_D^{21} = 1.4508$. – IR. (film): 3030, 2960, 1700, 1645, 1580, 1420, 1390, 1370, 1320, 1250, 1150, 1080, 1050, 1000, 950, 850, 780, 720, 710, 670. – ^{1}H-NMR. (CCl_4): 0.0 (*s*, 9 H, 3 H_3C–si); 1.1 (*s*, 9 H, 3 H_3C–C(2)); 1.4 (*d*, $J = 7.5$, 2 H, 2 H–C(7)); 3.1 (*d*, $J = 5$, 2 H, 2 H–C(4)); 5.4 (*m*, 2 H, 2 CH = CH). – MS.: 212 (3), 197 (7), 155 (48), 143 (22), 127 (4), 97 (4), 85 (4), 73 (100), 45 (17), 41 (17).

$C_{12}H_{24}OSi$ (212.4) Calc. C 67.86 H 11.39% Found C 67.71 H 11.59%

*7-(*t*-Butyldimethylsilyl)-2,2-dimethyl-5-hepten-3-one* (**3bb**). The solution of the dianion **1b** (10 mmol) in THF was treated with *t*-butyldimethylchlorosilane (1.8 g, 12 mmol) in THF (5 ml) at –78° and stirred at –78° for 1 h and at RT. for ½ h. The reaction was quenched with water and the mixture was extracted with pentane (3 × 100 ml). The combined organic phase was washed twice with cold 10%-$NaHCO_3$-solution and once with cold water. After drying ($MgSO_4$) the solvent was removed under reduced pressure to give a crude product (2.84 g). It was purified by passing over silica gel (80 g) using ether/pentane 5:95 as solvent for elution, to give an oily product (1.11 g). After distillation **3bb** (0.98 g, 39%) was isolated as colorless oil, b.p. 90°/0.006 Torr; $n_D^{21} = 1.4608$.– Rf 0.7 (ether/pentane 2:3). (By reacting with 20 mmol *t*-butyldimethylchlorosilane **3bb** was obtained in 36% yield). – IR. (film): 3030, 2960, 2940, 2860, 1710, 1640, 1470, 1390, 1365, 1315, 1250, 1150, 1075, 1000, 945, 840, 810, 750, 680. – ^{1}H-NMR. (CCl_4): 0 (s, 6 H, 2 H_3C–Si); 0.96 (*s*, 9 H, 3 H_3C–C–Si); 1.2 (*s*, 9 H, 3 H_3C–C(2)); 2.5 (*d*, $J = 7.5$, 2 H, 2 H–C(7)); 3.16 (*d*, $J = 5$, 2 H, 2 H–C(4)); 5.63 (*m*, 2 H, CH = CH).

$C_{15}H_{30}OSi$ (254.5) Calc. C 70.79 H 11.88% Found C 70.88 H 11.94%

1.3. *Preparation of the acylation product* **5**. – *2,2,9-Trimethyl-5-decene-3,8-dione* (**5**). The cold (–78°) solution of the dianion **1b** (10 mmol) in THF was treated with methyl isobutyrate (0.82 g, 8 mmol) and stirred for 3 h (–78° to RT.). It was cooled to –78°, quenched with acetic acid (2 ml), poured into water and extracted with pentane. The organic phase was washed several times with water and once with sat. NaCl-solution. After drying ($MgSO_4$) the solvent was removed under reduced pressure to give a crude product which on bulb-tube distillation furnished **5** (0.41 g, 24%) as yellowish oil, b.p. 90°/0.005 Torr; $n_D^{22} = 1.4590$.

When the dianion **1b** (10 mmol) was reacted with methyl isobutyrate (1.122 g, 12 mmol) in presence of HMPT (3.48 ml, 20 mmol) at –78° (1 h) it furnished **5** in 23% yield. – IR. (film): 3030, 2970, 2870, 1710, 1625, 1480, 1465, 1380, 1365, 1310, 1005, 940, 840, 780. – ^{1}H-NMR. (CCl_4): 1.06 (*d*, $J = 7$, 6 H, 2 H_3C–C(9)); 1.13 (*s*, 9 H, 3 H_3C–C(2)); 2.6 (*m*, 1 H, H–C(9)); 3.1 and 3.16 (2*d*, $J \approx 5$, 4 H, 2 H–C(7) and 2 H–C(4)); 5.7 (*m*, 2 H, CH = CH). – MS.: 210 (10), 153 (6), 125 (8), 107 (10), 85 (16), 71 (41), 57 (100), 43 (53).

$C_{13}H_{22}O_2$ (210.3) Calc. C 74.24 H 10.54% Found C 73.55 H 10.60%

2. Reactions of dianions of type *1* *with aldehydes, ketones and enones.* – 2.1. *Reactions of* **1a, 1b** *and* **1d** *with aldehydes, ketones and enones.* – 2.1.1. *General procedure.* The solution of the dianion **1b** or **1d** (10 mmol) in THF was cooled to –78°. The electrophile (10 mmol) was added in presence or absence of HMPT (20 mmol). The dianion **1a** (10 mmol) was reacted similarly with electrophile (6 mmol) in absence of HMPT. In case of the dianion **1d**, after addition of the electrophile, the reaction mixture was stirred for 3 to 4 h (–78° to RT.) and in case of the dianion **1a** and **1b** it was stirred at –78° for 2–3 h. It was then quenched at –78° with acetic acid and poured into water. The mixture was extracted three times with ether. The organic layer was dried over $MgSO_4$. The crude product obtained, after removal of solvent under reduced pressure, was chromatographed over silica gel (40 g, per gram of crude product), with ether/pentane 1:4. In all cases in addition to the product, the unreacted starting compound, its double-bond shifted isomer, and in some cases the dimers were present as impurities. For product yields see *Table 1*.

2.1.2. *Data of the products* **6a–d, 13b** *and* **13d**. – (E)-*7-Hydroxy-7-phenyl-4-hepten-2-one* (**6aa**). – Rf 0.16 (ether/pentane 1:1). – IR. (film): 3200–3600, 1710, 1670, 1600, 1490, 1450, 1160, 1050, 880, 760, 700. – ^{1}H-NMR. (CCl_4): 2.0 (*s*, 3 H, 3 H–C(1)); 2.4 (br. *t*, $J \approx 6$, 2 H, 2 H–C(6)); 2.37 (br. *s*, 1 H, OH); 3.03 (*d*, $J = 6$, 2 H, 2 H–C(3)); 4.6 (*t*, $J = 6.5$, 1 H, H–C(7)); 5.56 (*m*, 2 H, CH = CH); 7.25 (br. *s*, 5 H, aromat. H).

$C_{13}H_{16}O_2$ (204.3) Calc. C 76.44 H 7.90% Found C 75.86 H 7.90%

6-(1-Hydroxycyclohexyl)-4-hexen-2-one (**6ab**). This compound could not be isolated in pure form. The spectroscopic yield is reported in *Table 1*.

(E)-*7-Hydroxy-7-phenyl-4-octen-2-one* (**6ac**). Obtained as oil. – IR. (film): 3200–3600, 3030, 2980, 2940, 1710, 1640, 1600, 1495, 1450, 1360, 1260, 1240, 1165, 1070, 1030, 950, 915, 870, 770, 705. – ^{1}H-NMR. (CCl_4): 1.53 (*s*, 3 H, 3 H–C(8)); 2.13 (*s*, 3 H, 3 H–C(1)); 2.46 (*d*, *J*=6, 2 H, 2 H–C(6)); 2.9 (br. *s*, 1 H, OH); 3.03 (*d*, *J*=6, 2 H, 2 H–C(3)); 5.5 (*m*, 2 H, CH=CH); 7.33 (*m*, 5 H, aromat. H).

$C_{14}H_{18}O_2$ (218.3) Calc. C 77.03 H 8.31% Found C 76.12 H 8.21%

(E)-*7-Hydroxy-7,7-diphenyl-4-hepten-2-one* (**6ad**). For experimental procedure and physical properties *cf.* [1].

(E)-*8-Hydroxy-2,2-dimethyl-5-decen-3-one* (**6ba**). Propanal was added to the dianion in presence of HMPT to give **6ba**, b.p. 100°/0.006 Torr, colorless oil, n_D^{21} = 1.4612, Rf 0.25 (ether/pentane 2:3). – IR. (film): 3200–3600, 1705, 1655, 1480, 1460, 1395, 1370, 1315, 1110, 1070, 1020, *980*, 940, 860, 790, 700. – ^{1}H-NMR. (CCl_4): 0.9 (*t*, *J*=7, 3 H, 3 H–C(10)); 1.1 (*s*, 9 H, 3 H_3C–C(2)); 1.4 (*m*, 2 H, 2 H–C(9)); 2.06 (*m*, 2 H, 2 H–C(7)); 2.2 (br. *s*, 1 H, OH); 3.26 (*d*, *J*=5, 2 H, 2 H–C(4)); 3.4 (*qi*, *J*=6, 1 H, H–C(8)); 5.33–5.57 (*m*, 2 H, CH=CH). – ^{13}C-NMR. ($CDCl_3$): 26.33 (C(1)); 44.44 (C(2)); 214.0 (C(3)); 128.97 and 125.59 (C(5,6)); 72.30 (C(9)); 10.04, 29.8 and 35.15 (C(4,7,10)). – MS.: 198 (0.34), 180 (0.6), 169 (2.2), 140 (7.8), 123 (7), 95 (11), 85 (28.15), 81 (15.6), 57 (100), 41 (31.25).

$C_{12}H_{22}O_2$ (198.3) Calc. C 72.68 H 11.18% Found C 72.97 H 11.43%

(E)-*8-Hydroxy-2,2,9-trimethyl-5-decen-3-one* (**6bb**). 2-Methylpropanal was added in presence of HMPT to give **6bb**; b.p. 100°/0.006 Torr, colorless oil, n_D^{22} = 1.4617, Rf 0.33 (ether/pentane 2:3). – IR. (film): 3200–3600, 1710, 1655, 1480, 1395, 1375, 1315, 1070, 1010, *950*, 870, 850, 790, 705. – ^{1}H-NMR. (CCl_4): 0.9 (*d*, *J*=6, 6 H, 2 H_3C–C(9)); 1.1 (*s*, 9 H, 3 H_3C–C(2)); 1.6 (*m*, 1 H, H–C(9)); 2.06 (*t*, *J*≈6, 2 H, 2 H–C(7)); 2.23 (br. *s*, 1 H, OH); 3.1–3.33 (*m*, 3 H, H–C(8) and 2 H–C(4)); 5.36–5.73 (*m*, 2 H, CH=CH). ^{13}C-NMR. ($CDCl_3$): 26.37 (C(1)); 44.46 (C(2)); 214.03 (C(3)); 35.12 (C(4)); 125.01 and 129.61 (C(5,6)); 32.49 (C(7)); 75.71 (C(8)); 17.72, 18.80, 33.36 (2 H_3C–C(9) and C(9)). – MS.: 212 (0.02), 165 (0.4), 155 (0.2), 140 (5.2), 109 (5), 95 (9.7), 85 (19.1), 82 (7.4), 72 (69), 57 (100), 55 (11.4), 43 (10.2), 41 (19.4).

$C_{13}H_{24}O_2$ (212.2) Calc. C 73.53 H 11.39% Found C 73.51 H 11.37%

(E)-*8-Hydroxy-2,2-dimethyl-8-phenyl-5-octen-3-one* (**6bc**). Colorless oil, b.p. 130°/0.002 Torr n_D^{21} = 1.5188, Rf 0.27 (ether/pentane 2:3). – IR. (film): 3200–3600, 3025, 2970, 2870, 2910, 1950, 1870, 1810, 1700, 1650, 1600, 1490, 1480, 1450, 1395, 1370, 1315, 1200, 1060, *955*, 910, 875, 850, 760, 700. – ^{1}H-NMR. (CCl_4): 1.04 (*s*, 9 H, 3 H_3C–C(2)); 2.4 (*t*, *J*=6, 2 H, 2 H–C(7)); 2.7 (br. *s*, 1 H, OH); 3.13 (*d*, *J*=6, 2 H, 2 H–C(4)); 4.63 (*t*, *J*=7, 1 H, H–C(8)); 5.4–5.76 (*m*, 2 H, CH=CH), 7.25 (br. *s*, 5 H, aromat. H). – ^{13}C-NMR. ($CDCl_3$): 26.38 (C(1)); 44.33 (C(2)); 213.75 (C(3)); 37.81 (C(4)); 35.15 (C(7)); 73.32 (C(8)); 125.44, 125.81, 127.43, 128.39 and 144.28 (C(5), C(6), and aromat. C). – MS.: 189 (6.3), 147 (13.2), 143 (19.9), 140 (16.8), 129 (25), 107 (45), 105 (45.6), 85 (56), 79 (35), 77 (32.2), 57 (100), 41 (27).

$C_{16}H_{22}O_2$ (246.3) Calc. C 78.01 H 9.00% Found C 77.59 H 8.99%

(E)-*8-Hydroxy-2,2,8-trimethyl-5-nonen-3-one* (**6bd**). Colorless oil, b.p. 100°/0.008 Torr, $n_D^{21.5}$ = 1.4608, Rf 0.23 (ether/pentane 2:3). – IR. (film): 3200–3600, 2990, 2680, 1710, 1650, 1480, 1395, 1370, 1220, 1150, 1075, 1015, *985*, 950, 910, 850, 800, 700. – ^{1}H-NMR. (CCl_4): 1.13 (*s*, 9 H, 3 H_3C–C(2)); 1.16 (*s*, 6 H, 2 H_3C–C(8)); 1.8 (br. *s*, 1 H, OH); 2.23 (*d*, *J*=5, 2 H, 2 H–C(7)); 3.2 (*d*, *J*=5, 2 H, 2 H–C(4)); 5.43–5.8 (*m*, 2 H, CH=CH). – MS.: 140 (7.1), 123 (64), 96 (21.4), 95 (10.3), 86 (10.3), 85 (33.6), 81 (20.7), 59 (37.6), 57 (100), 43 (18.4), 41 (27).

$C_{12}H_{22}O_2$ (198.3) Calc. C 72.68 H 11.18% Found C 72.20 H 11.20%

8-(t-Butyl)-8-hydroxy-2,2-dimethyl-5,11-dodecadien-3-one (**6be**). Oil, n_D^{21} = 1.4775, Rf 0.51 (ether/pentane 2:3). – IR. (film): 3300–3640, 3080, 3030, 2965, 2880, 1710, 1640, 1480, 1395, 1370, 1320, 1210, 1074, 1010, 910, 795. – ^{1}H-NMR. (CCl_4): 0.93 (*s*, 9 H, 3 H_3C–C–C(8)); 1.13 (*s*, 9 H, 3 H_3C–C(2)); 1.4–1.8 (*m*, 3 H, OH and 2 H–C(9)); 1.93–2.36 (*m*, 4 H, 2 H–C(7) and 2 H–C(10)); 3.2 (*d*, *J*=6, 2 H, 2 H–C(4)); 4.83 and 5.63 (*m*, 5 H, olefin. H). – MS.: 280 (0.2), 265 (0.7), 223 (27.2), 123 (15), 85 (45.7), 57 (100), 43 (41.5).

$C_{18}H_{32}O_2$ (280.4) Calc C 77.09 H 11.50% Found C 76.95 H 11.33%

(E)-*7-(1-Hydroxycyclohexyl)-2,2-dimethyl-5-hepten-3-one* (**6bf**). B.p. 100°/0.002 Torr, n_D^{20} = 1.4843, Rf 0.3 (ether/pentane 2:3). – IR. (film): 3200–3600, 2940, 2860, 1710, 1650, 1480, 1450, 1400, 1370, 1320, 1260, 1150, 1070, 970 (trans-CH=CH), 910, 880, 795, 755, 700. – ^{1}H-NMR. (CCl_4): 1.13 (*s*, 9 H, 3 H_3C–

C(2)); 1.0–1.8 (*m*, OH and methylene H); 2.06 (*d*, *J*=5, 2 H, 2 H–C(7)); 3.2 (*d*, *J*=5, 2 H, 2 H–C(4)); 5.43–5.83 (m, *J* (trans)=11, 2 H, CH=CH). – ^{13}C-NMR. ($CDCl_3$): 26.36 (C(1)); 44.48 (C(2)); 214.82 (C(3)); 37.58 (C(4)); 125.59 and 127.56 (C(5,6)); 35.22 (C(7)); 71.38 (C(1')); 22.29, 25.89, 40.3 (C(2'–6')). – MS.: 238 (0.8), 140 (8.9), 121 (8.4), 99 (39.8), 85 (44.4), 81 (35.1), 57 (100), 55 (20.3), 41 (25).

$C_{15}H_{26}O_2$ (238.4) Calc. C 75.58 H 11.00% O 13.42 Found C 75.47 H 10.92 O 13.26%

(E)-*8-Hydroxy-2,2,8-trimethyl-5,9-decadien-3-one* (**6bg**). B.p. 90°/0.004 Torr, $n_D^{20.5}$=1.4706, Rf 0.28 (ether/pentane 2:3). The 1,4-adduct (**13a**) was isolated in about 5% yield and **6bg** in 23% yield. **6bg**: – IR. (film): 3200–3600, 3090, 3030, 2970, 2930, 2910, 2880, 1710, 1640, 1480, 1395, 1370, 1320, 1110, 1070, 1000, 920, 880, 800, 705. – ^{1}H-NMR. (CCl_4): 1.16 (*s*, 9 H, 3 H_3C–C(2)); 1.3 (*s*, 3 H, H_3C–C(8)); 2.2 (*s*, 1 H, OH); 2.3 (*d*, *J*=6, 2 H, 2 H–C(7)); 3.3 (*d*, *J*=6, 2 H, 2 H–C(4)); 5.0–5.4 (*m*, 2 H, 2 H–C(10)); 5.46–6.2 (*m*, 3 H, H–C(5,6,9)). – MS.: 210 (0.5), 193 (3.3), 140 (12.5), 93 (31), 85 (36.2), 71 (36.2), 57 (100), 41 (28.1).

$C_{13}H_{22}O_2$ (210.3) Calc. C 74.24 H 10.54% Found C 74.20 H 10.67%

(E)-*7-(1-Hydroxy-2-cyclohexen-1-yl)-2,2-dimethyl-5-hepten-3-one* (**6bh**) *and 2,2-dimethyl-7-(3-oxocyclohexyl)-5-hepten-3-one* (**13c**). The reaction of the dianion with cyclohexenone gave the 1,2-adduct **6bh** (17%) along with the 1,4-adduct **13c** (22%). When the rection was carried out in presence of HMPT it furnished **6bh** in 15% yield and **13c** in 28% yield.

Compound **6bh**. B.p. 120°/0.004 Torr, $n_D^{20.5}$=1.4953, Rf 0.24 (ether/pentane 2:3). – IR. (film): 3200–3600, 3030, 2980, 2900. 2880, 2840, 1710, 1650, 1480, 1395, 1370, 1320, 1170, 1075, 990, 950, 920, 890, 850, 800, 740, 670. – ^{1}H-NMR. (CCl_4): 1.15 (*s*, 9 H, 3 H_3C–C(2)); 1.63 (*m*, 4 H, 2 H–C(5',6')); 2.0 (*m*, 2 H, 2 H–C(7 or 4')); 2.2 (*d*, *J*=6, 2 H, 2 H–C(4' or 7); 3.22 (*d*, *J*=6, 2 H, 2 H–C(4)); 5.4–5.85 (*m*, 4 H, 2 CH=CH). – MS.: 236 (0.3), 218 (2.8), 161 (3.2), 133 (10.4), 119 (8.1), 97 (100), 91 (15.7), 85 (14.5), 79 (16.2), 57 (58), 41 (20.8).

$C_{15}H_{24}O_2$ (236.3) Calc. C 76.22 H 10.24% Found C 76.06 H 10.36%

Compound **13c**. B.p. 120°/0.004 Torr, $n_D^{20.5}$=1.4827, Rf 0.3 (ether/pentane 2:3). – IR. (film): 3030, 2900–2970, 2880, 1710, 1650, 1480, 1450, 1400, 1370, 1350, 1315, 1230, 1075, 1010, 945, 870, 850, 790, 755, 710. – ^{1}H-NMR. (CCl_4): 1.13 (*s*, 9 H, 3 H_3C–C(2)); 1.2–2.5 (br. *m*, 11 H); 3.16 (*d*, *J*=6, 2 H, 2 H–C(4)); 5.26–5.8 (*m*, 2 H, CH=CH). – MS.: 236 (0.9), 218 (0.4), 179 (8.1), 110 (9.1), 97 (35.7), 85 (20.4), 57 (100), 55 (10.6), 41 (33.9).

$C_{15}H_{24}O_2$ (236.3) Calc. C 76.22 H 10.24% Found C 76.04 H 10.32%

(E)-*7-(1-Hydroxy-2-cycloheptен-1-yl)-2,2-dimethyl-5-hepten-3-one* (**6bi**) *and 2,2-dimethyl-7-(3-oxocycloheptyl)-5-hepten-3-one* (**13d**). The 1,2-addition product **6bi** was obtained in 28% yield along with the 1,4-addition product **13d** (8%). *Data of* **6bi.** B.p. 120°/0.002 Torr, n_D^{21}=1.4980, Rf 0.24 (ether/pentane 2:3). – IR. (film): 3200–3600, 3020, 2970, 2930, 2870, 1710, 1650, 1480, 1450, 1395, 1370, 1320, 1225, 1070, 950, 865, 760, 695. – ^{1}H-NMR. (CCl_4): 1.13 (*s*, 9 H, 3 H_3C–C(2)); 1.4–2.4 (br. *m*, 11 H); 3.23 (*d*, *J*=6, 2 H, 2 H–C(4)); 5.43–5.83 (*m*, 4 H, 2 CH=CH). – MS.: 250 (4), 232 (14), 147 (29.4), 132 (11.6), 111 (43.7), 107 (12.2), 105 (14.2), 93 (17.6), 91 (31.2), 85 (13.5), 81 (13.1), 79 (19.4), 77 (11.2), 67 (15.3), 57 (100), 55 (14.5), 41 (25.5).

$C_{16}H_{26}O_2$ (250.4) Calc. C 76.75 H 10.47% Found C 76.63 H 10.59%

Data of **13d.** B.p. 120°/0.002 Torr n_D^{21}=1.4868, Rf 0.31 (ether/pentane 2:3). – IR. (film): 3030, 2980, 2940, 2890, 1705, 1650, 1480, 1450, 1400, 1370, 1320, 1250, 1200, 1080, 1010, 950, 850, 790, 715. – ^{1}H-NMR. (CCl_4): 1.13 (*s*, 9 H, 3 H_3C–C(2)); 1.0–2.3 *(m);* 2.45 *(m);* 3.23 (*d*, *J*=6, 2 H, 2 H–C(4)); 5.33–5.86 (*m*, 2 H, CH=CH). – MS.: 250 (5.6), 193 (5.9), 175 (6.25), 166 (5.22), 147 (5.9), 123 (6.25), 111 (29.8), 85 (23.6), 67 (11.8), 57 (100), 41 (30).

$C_{16}H_{26}O_2$ (250.4) Calc. C 76.75 H 10.47% Found C 76.43 H 10.63%

2,2-Dimethyl-7-(3-oxocyclopentyl)-5-hepten-3-one (**13b**). Reaction of cyclopentenone furnished exclusively the 1,4-adduct **13b** in 24% yield, b.p. 120°/0.002 Torr, n_D^{21}=1.4772, Rf 0.28 (ether/pentane 2:3). – IR. (film): 3030, 2870–2970, 1740, 1708, 1640, 1480, 1400, 1368, 1320, 1280, 1240, 1165, 1070, 1010, 930, 870, 850, 790, 710. – ^{1}H-NMR. (CCl_4): 1.13 (*s*, 9 H, 3 H_3C–C(2)); 1.3–2.5 (br. *m*, 9 H); 3.16 (*d*, *J*=6, 2 H, 2 H–C(4)); 5.33–5.8 (*m*, 2 H, CH=CH). – MS.: 222 (6.1), 204 (0.8), 165 (12.5), 138 (8.5), 122 (6.8); 109 (10.9), 95 (20.5), 85 (39.7), 67 (9.7), 57 (100), 41 (35.9).

$C_{14}H_{22}O_2$ (222.3) Calc. C 75.63 H 9.97% Found C 75.40 H 10.04%

(E)-*8-Hydroxy-2,2-dimethyl-8,8-diphenyl-5-octen-3-one* (**6bj**). For experimental details and physical properties *cf.* [1].

2,8-Dihydroxy-2-methyl-8,8-diphenyl-5-octene-3-one (**6ca**). The trianion **1c** (5 mmol, in 20 ml THF), was reacted with benzophenone (5 mmol) at –78°. After 1 h at –78° (deep blue mixture) the reaction was quenched with 2.5 ml acetic acid. Usual workup and chromatography over silica gel yielded 0.96 g of the major isomer, 0.06 g of the minor isomer, and 0.13 g of a mixture of both (total yield: 70%), all fractions as viscous oils. – ^{1}H-NMR. (CCl_4): *major isomer*: 1.28 (*s*, 6 H, 2 H_3C–C(2)); 2.95 (br. *d*, J=6,5, 2 H, 2 H–C(7)); 3.3 (br. *d*, J=6, 2 H, 2 H–C(4)); 3.45 (br. *s*, 2 H, 2 (OH)); 5.25–5.75 (*m*, 2 H, HC=CH); 7.0–7.45 (*m*, 10 H, aromat. H); *minor isomer*: 1.18 (*s*, 6 H, 2 H_3C–C(2)); 2.95 (br. *d*, J=6, 2 H, 2 H–C(7); 3.13 (br. *d*, J=6, 2 H, 2 H–C(4)); 3.9 (br. *s*, 2 H, 2 OH); 5.15–5.8 (*m*, 2 H, HC=CH); 7.05–7.5 (*m*, 10 H, aromat. H). – ^{13}C-NMR. ($CDCl_3$): *major isomer*: 26.36 (C(1)); 76.65 (C(2)); 213.07 (C(3)); 34.60 (C(4)); 125.23, 125.97, 126.82, 128.10, 128,35, 146.60 (C(5), C(6) and aromat. C); 40.04 (C(7)); 77.45 (C(8)); *minor isomer*: 39.49 (C(4)); 45.35 (C(7)).

(E)-*6-Hydroxyl-phenyl-3-octen-1-one* (**6da**). M.p. 36–38° (from ether/pentane 1:4). This compound was obtained by carrying out the reaction in presence of HMPT. – IR. (KBr): 3430, 1685, 1600, 1580, 1450, 1210, 980 (*trans*-CH=CH), 765, 690. – ^{1}H-NMR. ($CDCl_3$): 0.92 (*t*, J=7, 3 H, 3 H–C(8)); 1.44 (*m*, 2 H, 2 H–C(7)); 2.28 (*m*, 2 H, 2 H–C(5)); 3.4 (br. *s*, 1 H, OH); 3.66 (*m*, 1 H, H–C(6)); 3.83 (*d*, J=6, 2 H, 2 H–C(2)); 5.68 (m, *J(trans)*=16, 2 H, CH=CH); 7.64 and 8.06 (*m*, 5 H, aromat. H).

$C_{14}H_{18}O_2$ (218.3) Calc. C 77.06 H 8.26% Found C 76.40 H 8.27%

(E)-*6-Hydroxy-7-methyl-1-phenyl-3-octen-1-one* (**6db**). Oil, n_D^{20}=1.5312, Rf 0.23 (ether/pentane 2:3). – IR. (film): 3450, 2950, 1680, 1595, 1580, 1450, 1270, 1205, 980 (trans-CH=CH), 750, 690. – ^{1}H-NMR. (CCl_4): 0.92 (*d*, J=7, 6 H, 2 H_3C–C(2)); 1.6 (*m*, 1 H, H–C(7)); 2.18 (*m*, 2 H, 2 H–C(5)); 2.85 (br. *s*, 1 H, OH); 3.28 (*m*, 1 H, H–C(6)); 3.62 (*d*, J=6, 2 H, 2 H–C(2)); 5.62 (m, *J(trans)*=15, 2 H, CH=CH); 7.4 and 7.92 (*m*, 5 H, aromat. H).

$C_{15}H_{20}O_2$ (232.3) Calc. C 77.54 H 8.62% Found C 77.61 H 8.62%

(E)-*6-Hydroxy-1,6-diphenyl-3-hexen-1-one* (**6dc**). This compound was obtained by reacting the dianion with benzaldehyde in presence of HMPT, m.p. 93–95° (from ether/pentane 3:7). – IR. (KI): 3245, 3030, 1685, 1595, 1580, 1450, 1493, 1405, 1360, 1330, 1290, 1210, 1040, 980 (trans-CH=CH), 950, 750, 700. – ^{1}H-NMR. ($CDCl_3$): 2.2 (br. *t*, $J\approx$5, 2 H, 2 H–C(5)); 3.1 (*d*, J=5.5, 2 H, 2 H–C(2)); 4.4 (*t*, J=6, 1 H, H–C(6)); 5.44–6.1 (*m*, *J(trans)*=16.5, 2 H, CH=CH); 7.02, 7.18 and 7.66 (*m*, 10 H, aromat. H).

$C_{18}H_{18}O_2$ (266.3) Calc. C 81.17 H 6.81% Found C 81.07 H 6.66%

(E)-*5-(1-Hydroxycyclohexyl)-1-phenyl-3-penten-1-one* (**6dd**). M.p. 54–55° (from ether/pentane 1:9), Rf 0.16 (ether/pentane 2:3). – IR. (KBr): 3500, 2930, 2860, 1680, 1600, 1580, 1445, 1210, 980 (trans-CH=CH), 750, 690. – ^{1}H-NMR. (CCl_4): 1.1–1.8 (br. *m*, 10 H, methylene H); 2.06 (*d*, J=6, 2 H, 2 H–C(5)); 3.64 (*d*, J=6, 2 H, 2 H–C(2)); 3.25 (br. *s*, 1 H, OH); 5.8 (*m*, *J(trans)*=14, 2 H, CH=CH); 7.5 and 8.0 (*m*, 5 H, aromat. H).

$C_{17}H_{22}O_2$ (258.4) Calc. C 79.07 H 8.52% Found C 78.92 H 8.46%

(E)-*6-Hydroxy-1,6-Diphenyl-3,9-decadien-1-one* (**6de**). This reaction was carried out in presence of HMPT. M.p. 63–65° (from ether/pentane 1:9), Rf 0.34 (ether/pentane 2:3). – IR. (KI): 3480, 1680, 1635, 1595, 1580, 1490, 1450, 1405, 1230, 1215, 1060, 975 (trans-CH=CH), 915, 760, 700. – ^{1}H-NMR. ($CDCl_3$): 1.9 (*d*, J=5.5, 2 H, 2 H–C(5)); 1.8–2.36 (*m*, 2 H, 2 H–C(7)); 2.66 (*m*, 2 H, 2 H–C(8)); 3.6 (*d*, J=5.5, 2 H, 2 H–C(2)); 4.84 (*m*, 2 H, 2 H–C(10)); 5.1–6.2 (*m*, J=16, 3 H, H–C(3,4,9)); 7.02, 7.18 and 7.66 (*m*, 10 H, aromat. H).

$C_{22}H_{22}O_2$ (318.4) Calc. C 82.50 H 7.50% Found C 82.37 H 7.42%

(E)-*6-Hydroxy-1,6,6-triphenyl-3-hexen-1-one* (**6df**). For experimental procedure and physical data *cf.* [1].

2.2. *Reactions of* **1e** *and* **1f** *with aldehydes and ketones.* – 2.2.1. *General procedure.* The solution of the dianion (10 mmol) in THF was cooled to –78° and treated with electrophiles (10 mmol) in presence or absence of HMPT (20 mmol). After addition of the electrophiles, the yellow solution obtained, was stirred for 2 h at –78° and quenched with acetic acid. It was poured into water and extracted with pentane. After drying over $MgSO_4$, the solvent was removed under reduced pressure to give a residue which was purified by passing through a column of silicagel, using pentane and ether/pentane as solvent for elution. All the products in this series were found to be thermally unstable and could not be distilled.

The products after chromatography were analyzed directly. In all these cases along with the major d^5-products, some minor d^3-products were also isolated. The order of elution of the d^5- and d^3-adducts is mentioned in each case. For yields and d^5/d^3-ratios see *Table 1.*

2.2.2. *Preparation and data of the products* **6e, 6f, 8, 9, 10, 12.** – *Methyl 6-hydroxy-6-phenyl-3-hexenedithioate* (**6ea**). The crude product obtained was purified by passing over silicagel using ether/pentane 1:4 as solvent for elution. Viscous orange oil. – IR. (film): 3400, 3025, 2918, 1600, 1490, 1450, 1428, 1195–1250, 1140, 1030, 970 (*trans*-CH=CH); 915, 865, 770, 705. – ^{1}H-NMR. (CCl_4): 2.2 (br. *s*, 1 H, OH); 2.4 (*t*, *J*=6, 2 H, 2 H–C(5)); 2.58 (*s*, 3 H, H_3C–S); 3.66 (*d*, *J*=5.5, 2 H, 2 H–C(2)); 4.6 (br. *t*, *J*=6, 1 H, H–C(6)); 5.3–5.9 (*m*, 2 H, CH=CH), 7.23 (br. *s*, 5 H, aromat. H).

$C_{13}H_{16}OS_2$ (252.4) Calc. C 61.86 H 6.39 S 25.40% Found C 61.13 H 6.38 S 24.85%

Methyl 5-(1-hydroxycyclohexyl)-3-pentenedithioate (**6eb**). Viscous orange oil. – IR. (film): 3450, 2925, 2860, 1445, 1410, 1130, 1080–1020, 970 (trans CH=CH), 870. – ^{1}H-NMR. (CCl_4): 1.0–1.85 (*m*, 11 H,–$(CH2)_5$– and OH); 2.15 (*d*, *J*=5, 2 H, 2 H–C(5)); 2.6 (*s*, 3 H, H_3C–S); 3.67 (*d*, *J*=5, 2 H, 2 H–C(2)); 5.45–5.86 (*m*, 2 H, CH=CH).

Methyl 6-hydroxy-6,6-diphenyl-3-pentenedithioate (**6ec**). For experimental details and physical data *cf.* [1].

Isopropyl 6-hydroxy-3-octenedithioate (**6fa**). The crude product was purified by passing it through a column of silicagel and eluting with ether/pentane 1:9. The d^3-product was also isolated (~2%). – IR. (film): 3400, 3025, 2960, 2920, 2870, 1660, 1460, 1365, 1300, 1250–1210, 1160, 1050, 1015, 970 (trans-CH=CH), 865. – ^{1}H-NMR. (CCl_4): 0.93 (*t*, *J*=7, 3 H, H_3C–C(8)); 1.35 (*m*, 2 H, 2 H–C(7)); 1.37 (*d*, *J*=7, 6 H, 2 H_3C–C–S); 2.16 (*m*, 2 H, 2 H–C(5)); 3.46 (*m*, 1 H, H–C(6)); 3.6 (*d*, *J*=5, 2 H, 2 H–C(2)); 3.9 (*sept.*, *J*=7, 1 H, HCS); 5.33–5.86 (*m*, 2 H, CH=CH). – MS.: 232 (24), 189 (100), 171 (10), 157 (33), 131 (21), 97 (95), 91 (67), 69 (62), 55 (67), 43 (72).

$C_{11}H_{20}OS_2$ (232.4) Calc. C 56.85 H 8.67 S 27.59% Found C 56.60 H 8.77 S 26.43%

Isopropyl 6-hydroxy-7-methyl-3-octenedithioate (**6fb**). The crude product after chromatography over silicagel using ether/pentane 1:9 as solvent for elution furnished **7fb** and the d^3-adduct (~2%). – IR. (film): 3450, 2960, 2930, 2870, 1660, 1460, 1375, 1365, 1245, 1225, 1160, 1130, 1055, 1000, 970 (*trans*-CH=CH), 860. – ^{1}H-NMR. (CCl_4): 1.9 (*d*, *J*=7, 6 H, 2 H_3C–C(7)); 1.38 (*d*, *J*=7, 6 H, $(CH_3)_2CH$–S), 1.2–1.9 (*m*, 4 H, OH, H–C(7) and 2 H–C(5)); 3.26 (*m*, 1 H, H–C(6)); 3.6 (*d*, *J*=5, 2 H, 2 H–C(2)); 3.9 (*sept.*, *J*=7, 1 H, HCS); 5.35–5.86 (*m*, 2 H, CH=CH). – MS.: 246 (21), 203 (62), 185 (19), 171 (22), 110 (78), 95 (100), 83 (47), 69 (92), 55 (23), 43 (90).

$C_{12}H_{22}OS_2$ (246.4) Calc. C 58.49 H 8.99 S 26.02% Found C 59.07 H 8.96 S 25.30%

Isopropyl 6-hydroxy-7,7-dimethyl-3-octenedithioate (**6fc**). This compound was purified by chromatography over silicagel using ether/pentane 1:9 as solvent for elution. The d^3-adduct was isolated in ~2% yield. – IR. (film): 3500, 2960, 2870, 1665, 1640, 1480, 1460, 1398, 1385, 1365, 1300, 1240, 1180, 1160, 1140, 1070, 1055, 1010, 970, 860, 665. – ^{1}H-NMR. (CCl_4): 0.9 (*s*, 9 H, 3 H_3C–C(7)); 1.37 (*d*, *J*=7, 6 H, $(CH_3)_2CH$–S); 1.52 (br. *s*, 1 H, OH); 1.26–2.46 (*m*, 2 H, 2 H–C(5)); 3.16 (*d*×*d*, *J*=11 and 2, 1 H, H–C(6)); 3.6 (*m*, 2 H, 2 H–C(2)); 3.92 (*sept.* *J*=7, 1 H, HCS); 5.33–5.86 (*m*, 2 H, CH=CH). – MS.: 260 (28), 217 (86), 203 (22), 199 (28), 185 (58), 125 (67), 109 (75), 97 (86), 83 (100), 69 (36), 55 (58), 43 (86).

$C_{13}H_{24}OS_2$ (260.5) Calc. C 59.95 H 9.29 S 24.62% Found C 59.90 H 9.29 S 24.44%

Isopropyl 6-hydroxy-6-phenyl-3-hexenedithioate (**6fd**). It was purified by chromatography over silicagel using ether/pentane 1:4 as solvent for elution. The yield of d^3-adduct isolated was ~7% and of **7fd** 61%.

When this reaction was carried out in presence of HMPT, **6fd** was isolated in 73% yield and the d^3-adduct in *ca.* 4% yield. – IR. (film): 3400, 3030, 2960, 2925, 2860, 1600, 1490, 1450, 1383, 1365, 1130, 1050, 970 (*trans*-HC=CH), 860, 760, 700. – ^{1}H-NMR. (CCl_4): 1.4 (*d*, *J*=7, 6 H, $(CH_3)_2CH$–S_2); 1.87 (br. *s*, 1 H, OH); 2.42 (*t*, *J*=6, 2 H, 2 H–C(5)); 3.56 (*d*, *J*=5.5, 2 H, 2 H–C(2)); 3.9 (*sept.*, *J*=7, 1 H, $(CH_3)CH$–S); 4.62 (*t*, *J*=7, 1 H, H–C(6)); 5.33–5.86 (*m*, 2 H, CH=CH); 7.23 (br. *s*, 5 H, aromat. H).

$C_{15}H_{20}OS_2$ (280.4) Calc. C 64.24 H 7.19 S 22.87% Found C 64.15 H 7.04 S 22.70%

Isopropyl 6-hydroxy-6-methyl-3-heptenedithioate (**6fe**). This compound was obtained in 39% yield after purification over silicagel column on eluting with ether/pentane 15:85. The d^3-adduct was also isolated in ~6% yield. – IR. (film): 3400, 2970, 2930, 1460, 1365, 1215, 1160, 1130, 1052, 970 (trans-CH=CH), 905, 860. – ^{1}H-NMR. (CCl_4): 1.16 (*s*, 6 H, $(CH_3)_2CH$–S), 1.4 (*d*, *J*=7, 7 H, 2 H_3C–C(6); un-

der this signal lies a br. *s*, OH); 2.16 (*d*, *J*=5, 2 H, 2 H–C(5)); 3.65 (*d*, *J*=5, 2 H, 2 H–C(2); 3.95 (*sept.*, *J*=7, 1 H, $(CH_3)_2CH$–S); 5.4–5.86 (*m*, 2 H, CH=CH). – ^{13}C-NMR. ($CDCl_3$): 21.37 (*qa*, CH_3); 29.18 (*qa*, $(CH_3)_2$); 41.04 (*d*, CHS); 46.62 (*t*, CH_2); 55.26 (*t*, CH_2CS); 70.69 (*s*, C–O); 129 and 130, 138.84 (*s*, C=S). – MS.: 232 (30), 189 (48), 171 (21), 99 (36), 97 (48), 81 (48), 69 (33), 59 (70), 43 (100).

$C_{11}H_{20}OS_2$ (232.4) Calc. C 56.85 H 8.67 S 27.59% Found C 56.85 H 8.78 S 27.36%

Isopropyl 5-(1-hydroxycyclopentyl)-3-pentenedithioate (**6ff**). The crude product on chromatography over silicagel furnished the d^3-adduct (0.26 g, ~11%), and **6ff** (1.02 g, 44%). – IR (film): 3430, 2960, 2863, 1450, 1380, 1365, 1215, 1155, 1100, 1050, 1000, 970 (trans-CH=CH), 860. – ^{1}H-NMR. (CCl_4): 1.4 (*d*, *J*=7, 6 H, $(CH_3)_2$CH–S); 1.63 (br., 9 H, OH and $-(CH_2)_4-$); 2.25 (*d*, *J*=5, 2 H, 2 H–C(5)); 3.63 (*d*, *J*=5, 2 H, 2 H–C(2), 3.9 (*sept.*, *J*=7, 1 H, $(CH_3)_2CH$–S); 5.4–5.85 (*m*, 2 H, CH=CH).

$C_{13}H_{22}OS_2$ (258.4) Calc. C 60.42 H 8.58 S 24.81 Found C 60.46 H 8.81 S 24.43

Isopropyl 3-(1-hydroxycyclopentyl)-4-pentenedithioate (d^3-adduct **8a**). – IR. (film): 3450, 3080, 2960, 2870, 1635, 1460, 1440, 1418, 1383, 1363, 1325, 1230, N65, 990, 918, 825. – ^{1}H-NMR. (CCl_4): 1.33 and 1.35 (2*d*, *J*=7, 6 H, $(CH_3)_2$CH–S); 1.6 (br., 9 H, OH and $-(CH_2)_4-$); 2.78 (*m*, 1 H, H–C(3)); 3.1 (*m*, 2 H, 2 H–C(2)); 3.9 (*sept.*, *J*=7, 1 H, $(CH_3)_2CH$–S), 4.95 and 5.68 (*m*, 3 H, $CH=CH_2$).

$C_{13}H_{22}OS_2$ (258.4) Calc. C 60.42 H 8.58 S 24.81 Found C 60.67 H 8.43 S 22.76

Isopropyl 5-(1-hydroxycyclohexyl)-3-pentenedithioate (**6fg**). The crude product (1.34 g) obtained from **6f** (5 mmol) and cyclohexanone (5 mmol), was purified over silicagel column (80 g) using ether/pentane 15:85 as solvent for elution, to furnish the d^3-adduct (0.06 g, ~3%) and **6fg**. – IR. (film): 3450, 2930, 2860, 1450, 1380, 1365, 1160, 1130, 1100, 1055, 970 (trans-CH=CH), 865. – ^{1}H-NMR. (CCl_4): 1.4 (*d*, *J*=7); 1.1–1.73 (br. *m*, 11 H OH and $-(CH_2)_5-$); 2.13 (br. *d*, *J*=5, 2 H, 2 H–C(5)); 3.6 (br. *d*, *J*=5, 2 H, 2 H–C(2)); 3.9 (*sept.*, *J*=7, 1 H, $(CH_3)_2CH$–S); 5.4–5.83 (*m*, 2 H, CH=CH). – ^{13}C-NMR. ($CDCl_3$): 21.35, 22.23, 25.82, 37.52, 40.98 (*d*, CHS); 45.12 (*t*, CH_2C–O); 55.29 (*t*, CH_2CS); 71.34 (*s*, C–O), 129.43 and 129.94 (C=C), 138.81 (C=C), 138.81 (C=S). – MS.: 272 (39, M^+), 229 (100), 137 (73), 121 (47), 109 (31), 95 (45), 81 (18), 67 (24), 55 (31), 43 (36)

$C_{14}H_{24}OS_2$ (272.5) Calc. C 61.71 H 8.88 S 23.54 Found C 61.73 H 8.99 S 23.46

Isopropyl 3-(1-hydroxycyclohexyl)-4-pentenedithioate (d^3-adduct **8b**). – IR. (film): 3450, 3080, 2930, 2860, 1635, 1445, 1415, 1382, 1365, 1260, 1230, 1150, 1055, 992, 965, 913, 893, 853, 840, 790, 670. – ^{1}H-NMR. (CCl_4): 1.0–1.8 (br. *m*, 17 H, OH, $-(CH_2)_5-$, $(CH_3)_2$CH–S); 2.7 (*m*, 1 H, H–C(3)); 3.05 (*m*, 2 H, 2 H–C(2)); 3.88 (*sept.*, *J*=7, 1 H, $(CH_3)_2CH$–S); 4.93 and 5.58 (*m*, 3 H, $CH=CH_2$).

Isopropyl 6-hydroxy-6,6-diphenyl-3-hexene dithioate (**6fh**). For experimental details and physical data *cf.* [1].

8-Methyl-6-(methylthio)-1,1-diphenyl-7-thia-3,5-nonadien-1-ol (**9b**). To the solution of the dianion **1f** (10 mmol) in THF (at –78°) was added benzophenone. After stirring at –78° for 2 h, CH_3I (0.7 ml, 11 mmol) was added at –78° and the reaction mixture was allowed to come to 0°. The reaction mixture was stirred at 0° for 1 h and at RT. for 1 h. It was diluted with water and extracted with pentane. After usual workup it gave a crude product (3.72 g) which was chromatographed over silicagel (130 g). On elution with ether/pentane 1:9 it gave **9b** (2.96, 80%), m.p. 85–86°, white crystals. – IR. (KBr): 3480, 3030, 2960, 2925, 1635, 1600, 1490, 1450, 1368, 1240, 1205, 1155, 1055, 1010, 970, 900, 778, 755, 650, 605. – ^{1}H-NMR. ($CDCl_3$): 1,23 (*d*, *J*=7, 6 H, 2 H_3C–C(8)); 2.43 (*s*, 3 H, H_3C–S); 2.6 (*s*, 1 H, OH); 3.25 (*d*, *J*=7.5, 2 H, 2 H–C(2)); 3.45 (*sept.*, *J*=7, 1 H, $(CH_3)_2CH$–S); 5.75 (*t*×*d*, *J*=15 and 7.5, 1 H, H–C(3)); 6.6 (*d*, *J*=10, 1 H, H–C(5)); 6.96 (*d*×*d*, *J*=15 and 10, 1 H, H–C(4)); 7.5 (m, 10 H, aromat. H).

$C_{22}H_{26}OS$ (370) Calc. C 71.31 H 7.07 S 17.30% Found C 71.34 H 7.08 S 17.16%

8-Methyl-6-(methylthio)-1-phenyl-7-thia-3,5-hexadienyl acetate (**9a**). Following a procedure as for **9b**, the dianion **1f** (10 mmol) was reacted with benzaldehyde (1.01 ml, 10 mmol) and CH_3I (0.7 ml, 11 mmol). The reaction mixture was cooled to 0° and then treated with acetic anhydride (1.02 ml, 12 mmol) and stirred over night (~16 h). After usual workup it gave a crude product (3.85 g). On chromatographic purification over silicagel (140 g), using ether/pentane 1:9 as solvent for elution, **9a** (2.88 g, 77%) was obtained as viscous yellowish oil. – IR. (film): 3060, 3030, 2960, 2925, 2865, 1740, 1635, 1605, 1585, 1540, 1495, 1410–1470, 1370, 1235, 1155, 1025, 975, 890, 760, 700. – ^{1}H-NMR. (CCl_4): 1.23 (*d*, *J*=7, 6 H, 2 H_3C–C(8)); 2.0 (*s*, 3 H, CH_3COO); 2.25 (*s*, 3 H, H_3C–S); 3.62 (br. *t*, *J*=7.5, 2 H, 2 H–C(2)); 5.36–5.75 (*m*, 2 H, H–C(1) and H–C(3)); 6.42 (*d*, *J*=10, 1 H, H–C(5)); 6.62 (*d*×*d*, *J*=12 and 10, 1 H, H–C(4)); 7.25 (*s*, 5 H, aromat. H).

$C_{18}H_{24}O_2S_2$ (336.5) Calc. C 64.25 H 7.19 S 19.06% Found C 64.11 H 7.26 S 18.96%

6,8-Dimethyl-6-(methylthio)-1,1-diphenyl-7-thia-2,4-nonadien-1-ol (**10b**). To a cold mixture of LDA (5 mmol) and HMPT (2 ml) in THF (5 ml) was added a solution of **9b** (0.74 g, 2 mmol) in THF (5 ml). After complete addition of **9b** the reaction mixture became dark brown. In a period of 3 h the temperature was allowed to rise from –78° to 0°. It was then cooled to –78° and treated with CH_3I (0.3 g, ~2.1 mmol) in THF (1 ml). The resulting colorless solution was stirred in the cold (–78°) for 1 h and at RT. for 1 h. It was poured into a mixture of water and pentane and extracted with pentane. The crude product (0.7 g) obtained after usual workup was purified by passing over a silicagel (20 g) column. Elution with ether/pentane 1:9 furnished **10b** (0.58 g, 76%) as viscous oil. The *O*-methyl-(**10b**) was isolated in small amount.

Spectral data of **10b**: – IR. (film): 3450, 3060, 3030, 2980, 2920, 2860, 1600, 1490, 1445, 1380, 1365, 1240, 1155, 1120, 1070, 995, 905, 780, 760, 700. – ^{1}H-NMR. ($CDCl_3$): 1.27 and 1.3 (2*d*, J=7, 6 H, 2 H_3C–C(8)); 1.7 (*s*, 3 H, H_3C–C(6)); 2.05 (*s*, 3 H, H_3C–S); 2.4 (br. *s*, 1 H, OH); 2.96 (*sept.*, J=7, 1 H, $(CH_3)_2CH$–S); 5.75 (*m*, 1 H); 6.3 (*m*, 3 H); 7.33 (*m*, 10 H, aromat. H).

$C_{23}H_{28}OS_2$ (384.6) Calc. C 71.83 H 7.34 S 16.67% Found C 72.48 H 7.37 S 16.09%

Spectral data of O-*Methyl* **10b**: IR. (film): 3060, 3030, 2960, 2910, 2860, 2830, 1640, 1600, 1490, 1445, 1365, 1312, 1180, 1155, 1075, 995, 950, 790, 760, 700. – ^{1}H-NMR. ($CDCl_3$): 1.25 and 1.28 (2*d*, J=7, 6 H, $CH(CH_3)_2$); 1.7 (*s*, 3 H, CCH_3); 2.05 (*s*, 3 H, SCH_3); 2.97 (*m*, 1 H, CHS); 3.15 (*s*, 3 H, OCH_3); 5.73 (*d*) and 6.25 (*m*, olefin. H); 7.33 (*m*, 10 H, aromat. H).

6-Ethyl-8-methyl-6-methylthio-1,1-diphenyl-7-thia-2,4-nonadien-1-ol (**10c**). Following a similar procedure as for **10b**, the compound **9b** (0.74 g, 2 mmol) was reacted with LDA (5 mmol) and C_2H_5I (0.4 g, 2.5 mmol). After addition of C_2H_5I at –78° it was stirred at –78° for 30 min and at RT. for 3 h. The crude product (0.79 g) obtained after usual workup was chromatographed over silicagel (30 g). On elution with ether/pentane 1:9 **10c** (0.68 g, 85%) was isolated as viscous oil. – IR. (film): 3450, 3060, 3030, 2970, 2920, 2860, 1650, 1600, 1490, 1445, 1363, 1320, 1280, 1240, 1155, 1070, 1055, 1030, 995, 905, 780, 765, 705. – ^{1}H-NMR. ($CDCl_3$): 1.0 (*m*, 3 H, CH_2CH_3); 1.25 (*m*, 6 H, 2 H_3C–C(8)); 1.80 (*qa*, J=7, 2 H, CH_2CH_3); 2.0 (*s*, 3 H, H_3C–S); 2.26 (br. *s*, 1 H, OH); 2.95 (*sept.*, J=7, 1 H, $(CH_3)_2CH$–S); 5.6 (*m*, 1 H); 6.3 (*m*, 3 H); 7.3 (*m*, 10 H, aromat. H).

$C_{24}H_{30}OS_2$ (398.6) Calc. C 72.31 H 7.59 S 16.09% Found C 72.63 H 7.61 S 15.62%

7-Hydroxy-7,7-diphenyl-3,5-heptadien-2-one (**12a**). A mixture of **10b** (0.76 g, ~2 mmol), methyl iodide (1 ml), $CaCO_3$ (0.5 g) in water (4 ml), CH_3CN (5 ml) and THF (15 ml) was heated at 70–80° for 48 h. The reaction mixture was diluted with water and extracted with ether. After usual workup it gave a residue (0.51 g) which was purified by passing over a silicagel column (15 g). On elution with ether/pentane 1:9 **12a** (0.32 g, 57%) was isolated as faint yellow crystals, m.p. 128–130.5°. – IR. (KBr): 3400, 1675, 1655, 1640, 1600, 1490, 1450, 1370, 1265, 1215, 1170, 1130, 1065, 1000, 758, 748, 700, 665, 635. – ^{1}H-NMR. ($CDCl_3$): 2.25 (*s*, 3 H, H_3C–C(2)); 2.36 (*s*, 1 H, OH); 6.06–7.2 (*m*, 4 H, olefin. H); 7.36 (br. *s*, 10 H, aromat. H).

$C_{19}H_{18}O_2$ (278.3) Calc. C 81.98 H 6.52% Found C 81.74 H 6.62%

8-Hydroxy-8,8-diphenyl-4,6-octadien-3-one (**12b**). By using the procedure as for **12a**, on reacting **10c** (0.45 g, 1.13 mmol) with methyl iodide (0.64 g, 4.5 mmol) in water (2 ml), CH_3CN (2 ml) and THF (8 ml) **12b** (0.13 g, 39%) was obtained as faint yellow crystals, m.p. 110–112° (from ether/pentane 1:1). – IR. (KBr): 3400, 1660, 1640, 1600, 1486, 1445, 1355, 1200, 1160, 1130, 1065, 1000, 980, 865, 750, 740, 695. – ^{1}H-NMR. ($CDCl_3$): 1.1 (*t*, J=7, 3 H, H_3C–C(2)); 2.44 (*s*, 1 H, OH); 2.55 (*qa*, J=7, 2 H, 2 H–C(2)); 6.1–6.83 (*m*, 4 H, olefin. H); 7.36 (*m*, 10 H, aromat. H).

$C_{20}H_{20}O_2$ (292.4) Calc. C 82.15 H 6.89% Found C 81.98 H 6.93%

3. Ring opening of epoxides by the dianions of the type *1a–d* to furnish *14*. – 3.1. *General procedure.* The epoxide (10 mmol) was added to the cooled (–78°) solution of the dianion **1a, 1b** or **1d** in THF (10 mmol or 20 mmol). In case of **1c** a 10%-excess of the epoxide was employed. The reaction mixture was stirred at –50° to –30° for 4 h and then stirred over night (–30 to 0° or RT.) for 11–12 h. The reaction mixture was cooled to –78° and quenched with acetic acid (in case of **1a, 1b** and **1d**) or acidified to pH 6 with 1N HCl (in THF, 1:1). Sat. NaCl-solution was added, followed by three extractions with ether or pentane. The combined organic layers were washed with sat. salt solution. After drying over $MgSO_4$, the solvent was removed under reduced pressure to give an oily product. It was chromatographed over silicagel (40 g/g of crude product) and eluted successively with ether/pentane 1:9 and ether/pentane 3:7. For yields of the hydroxyketones **14** see *Table 2.*

These products isomerized and cyclized to the THP-derivatives when kept at RT. for more than three days or left on column for more than 24 h, but were stable when kept below 0°.

3.2. *Preparation and data of the hydroxy-enones* **14.** – *8-Hydroxy-8-methyl-4-nonen-2-one* (**14aa**). The compound **14aa** (3 g) was obtained by reacting the THF-solution of the dianion **1a** (20 mmol) with 2,2-dimethyloxirane (1.08 ml, 12 mmol), after chromatography over silicagel. It could not be isolated in pure form and was used as such for the cyclization (see below, **15aa**).

8-Hydroxy-8-phenyl-4-octen-2-one (**14ab**) *and 8-Hydroxy-7-phenyl-4-octen-2-one* (**14ac**). The dianion **1a** (20 mmol) in THF was treated with 2-phenyloxirane (1.44 ml, 12 mmol) to furnish **14ab** and **14ac**. These compounds could not be separated in pure forms and were used as such for the cyclization (see below, **15ab** and **15ac**).

(E)-*9-Hydroxy-2,2-dimethyl-5-decen-3-one* (**14ba**). Colorless oil, b.p. 70°/0.006 Torr. n_D^{21} = 1.4613, Rf 0.2 (ether/pentane 2:3). – IR. (film): 3100–3600, 3030, 2980, 2940, 2880, 1710, 1650, 1480, 1400, 1370, 1320, 1130, 1075, 1000, 940 (*trans*–CH=CH), 850, 800, 710. – ^{1}H-NMR. (CCl_4): 1.13 (*s*, 9 H, 3 H_3C–C(2)); 1.43 (*qa*, *J*=7, 2 H, 2 H–C(8)); 1.1 (*d*, *J*=7, 3 H, H_3C–C(9)); 2.0–2.4 (*m*, 3 H, OH and 2 H–C(7)); 3.2 (*d*, *J*=5, 2 H, 2 H–C(4)); 3.7 (*m*, 1 H, H–C(9)); 5.3–5.66 (*m*, *J* (trans)=11, 2 H, CH=CH). – ^{13}C-NMR. ($CDCl_3$): 26.40 (C(1)); 44.48 (C(2)); 213.96 (C(3)); 38.61 (C(4)); 122.35 and 132.53 (C(5,6)); 35.15 (C(7)); 67.21 (C(9)); 23.67 and 23.97 (C(8,10)). – MS.: 198 (0.3), 154 (3.6), 141 (6.1), 123 (5.9), 99 (61), 95 (20.3), 85 (21.8), 81 (17.2), 57 (100), 43 (12.5), 41 (22.6).

$C_{12}H_{22}O_2$ (198.3) Calc. C 72.68 H 11.18 O 16.14% Found C 72.26 H 11.23 O 16.68%

(+)-(S)-(E)-*9-Hydroxy-2,2-dimethyl-5-decen-3-one* (**14ba**): Colorless oil, 49% yield, $[\alpha]_D^{21}$ = +37.89° (*c*=1.945, benzene), n_D^{21} = 1.4622.

9-Hydroxy-2,2,9-trimethyl-5-decen-3-one (**14bb**). Colorless oil, b.p. 100°/0.01 Torr, n_D^{20} = 1.4596. – IR. (film): 3200–3600 br. (OH), 2980, 2880, 1710, 1655, 1480, 1395, 1370, 1320, 1220, 1140, 1085, 1060, 1020, *985*, 940, 910, 850, 800, 700. – ^{1}H-NMR. (CCl_4): 1.13 (*s*, 9 H, 3 H_3C–C(2)); 1.16 (*s*, 6 H, 2 H_3C–C(9)); 1.33–1.6 (*m*, 3 H, OH and 2 H–C(8)); 1.83–2.26 (*m*, 2 H, 2 H–C(7)); 3.2 (*d*, *J*=5, 2 H, 2 H–C(4)); 5.3–5.66 (*m*, 2 H, CH=CH). – ^{13}C-NMR. ($CDCl_3$): 26.47 (C(1)); 44.41 (C(2)); 213.6 (C(3)); 43.24 (C(4)); 122.06 and 132.87 (C(5,6)); 35.15 (C(7)), 70.81 (C(9)), 22.65 and 29.34 (C(8,10)). – MS.: 212 (0.1), 197 (3), 154 (2.2), 137 (6.1), 110 (10.6), 95 (22.7), 85 (14.7), 81 (15.3), 57 (100), 43 (16.1), 41 (25.4).

$C_{13}H_{24}O_2$ (212.3) Calc. C 73.53 H 11.39% Found C 73.43 H 11.47%

(E)-*7-(2-Hydroxycyclohexyl)-2,2-dimethyl-5-hepten-3-one* (**14bc**). Colorless oil; n_D^{20} = 1.4862; Rf 0.26 (ether/pentane 2:3). – IR. (film): 3200–3600, 2430, 2360, 1700, 1650, 1480, 1450, 1390, 1368, 1310, 1230, 1190, 1130, 1070, 1040, 1010, 935, 850. – ^{1}H-NMR. (CCl_4): 1.0 (*s*, 9 H, 3 H_3C–C(2)); 1.0–2.5 (*m*, 11 H, OH and 10 methylene H); 3.3 (br. *d*, *J*=6, 2 H, 2 H–C(4)); 3.13–3.3 (*m*, 1 H, H–C(2')); 5.43–5.85 (*m*, 2 H, CH=CH). – ^{13}C-NMR. ($CDCl_3$): 214.07 (C(3)), 122.94 and 131.20 C(5,6)), 74.29 (C(9)). – MS.: 238 (5.6), 220 (5.6), 181 (8.35), 163 (8.5), 136 (17.4), 121 (22), 81 (22), 67 (32.4), 57 (100), 41 (32.4).

$C_{15}H_{26}O_2$ (238.4) Calc. C 75.58 H 11.00 O 13.42% Found C 75.24 H 10.86 O 13.51%

(±)-2,9-Dihydroxy-2-methyl-5-decen-3-one (**14ca**). This compound was obtained as viscous oil. After keeping it at RT. and during the attempted distillation it cyclized to **15ca** *(3-hydroxy-3-methyl-1-(6-methyl-tetrahydropyran-2-yl)-2-butanone)*; it was, therefore, stored in a freezer. – IR. (film): 3400, 3020, 2970, 2930, 1708, 1455, 1370, 1355, 1190, 1130, 1065, 970, 900, 800. – ^{1}H-NMR. (CCl_4): 1.15 (*d*, *J*=6, 3 H, H_3C–C(9)); 1.35 (*s*, 6 H, 2 H_3C–C(3)); 1.5 (*m*, 2 H, 2 H–C(8)); 2.1 (*m*, 2 H, 2 H–C(7)); 2.6–3.0 (br. *s*, 2 H, 2 OH); 3.25 (*m*, 2 H, 2 H–C(4)); 3.7 (*sext.*, *J*=6, 1 H, H–C(9)); 5.52 (*m*, 2 H, CH=CH). – ^{13}C-NMR. ($CDCl_3$): major isomer: 26.49 (C(1)); 76.73 (C(2)); 213.23 (C(3)); 34.43 (C(4)); 132.94, 121.41 (C(5) and C(6)); 23.82 (C(7)); 38.40 (C(8)); 66.90 (C(9)); 23.41 (C(10)); minor isomer: 39.44 (C(4)); 134.53, 122.08 (C(5) and C(6)); 28.94 (C(7)); 67.14 (C(9)). – MS.: 157 (3), 139 (5), 124 (3), 114 (12), 96 (32), 95 (15), 81 (29), 67 (9), 59 (100), 54 (35), 43 (38), 31 (12), 18 (10).

$C_{11}H_{20}O_2$ (200.3) Calc. C 65.97 H 10.07% Found C 66.07 H 10.19%

(+)-(S)-*2,9-Dihydroxy-2-methyl-5-decen-3-one* (**14ca**). The solution of the dianion **1c** (20 mmol) in THF (100 ml) was cooled to –78° and treated with (–)-*(S)*-2-methyloxirane (1.52 g, 25.6 mmol). The reaction mixture was stirred between –50 to –30° for 4 h, and then stirred for a further period of 11 h (–30° to 10°). It was cooled to –70° and quenched with 1N HCl (containing equal volume of THF) till pH 6. It was transferred to the separating funnel. After removal of the organic phase the aq. phase was saturated with salt and extracted twice with ether. The combined organic phases were dried over $MgSO_4$. After

removal of solvent under reduced pressure an oily product was obtained and chromatographed over silicagel (100 g). The column was first eluted with ether/pentane 1:9 and then with ether/pentane 1:1. The product **14ca**, thus obtained (2.41 g, 60.2%) was a colorless oil, $n_D^{22} = 1.4727$, $[\alpha]_D^{20} = +21.75$ ($c = 1.08$, $CHCl_3$). – IR. (film): 3400 br., 2970, 2930, 2860, 1708, 1455, 1370, 1355, 1190, 1130, 1065, 970, 900, 840, 800. – ^{1}H-NMR. ($CDCl_3$): 1.2 (*d*, $J = 6$, 3 H, H_3C–C(9)); 1.4 (*s*, 6 H); 1.53 (*m*, 2 H, 2 H–C(8)); 1.7 (br. *s*, 2 H, exchanges with D_2O, 2 OH); 2.14 (*m*, 2 H, 2 H–C(7)); 3.37 (*m*, 2 H, 2 H–C(4)); 3.78 (*sext.*, 1 H, H–C(9)); 5.6 (m, 2 H, CH = CH). – MS. was identical with the authentic sample (±)-**14ca**.

2,9-Dihydroxy-2,8-dimethyl-5-decen-3-one (**14cb**). The solution of the dianion **1c** (20 mmol) in THF (100 ml) was cooled to –78° and treated with *trans*-2,3-dimethyloxirane (1.84 g, 25.6 mmol). The reaction mixture was stirred between –50 to –30° for 4 h and –30 to +10° for 15 h. The reaction mixture was cooled to –78°, quenched with 1N HCl and worked up as described for **14ca**. The crude product was chromatographed over silicagel and eluted successively with ether/pentane 1:9 and ether/pentane 1:1. The product **14cb** was obtained (2.55, 59%) as a colorless oil, $n_D^{24} = 1.4747$. – IR. (film): 3400, 3020, 2970, 2925, 2870, 1710, 1630, 1460, 1375, 1310, 1190, 1070, 982, 922, 891, 870, 800, 700. – ^{1}H-NMR. ($CDCl_3$): 0.9 (*d*, $J = 6$, 3 H, H_3C–C(8)); 1.16 (*d*, $J = 6$, 3 H, H_3C–C(9)); 1.41 (*s*, 6 H, 2 H_3C–C(2)); 3.15 (br. *s*, 2 H, exchanges with D_2O, 2 OH); 3.36 (*m*, 2 H, 2 H–C(4)); 3.76 (*m*, 1 H, H–C(9)); 5.63 (*m*, 2 H, CH = CH).

$C_{12}H_{22}O_3$ (214.3) Calc. C 67.25 H 10.35% Found C 67.15 H 10.23%

*2-Hydroxy-2-methyl-7-(*trans*-2-hydroxycyclohexyl)-5-hepten-3-one* (**14cc**). Viscous liquid, b.p. 140°/0.001 Torr. – IR. (film): 3400, 3020, 2980, 2930, 2855, 1710, 1450, 1370, 1310, 1190, 1135, 1065, 1040, 975, 935, 845, 825, 800, 710. – ^{1}H-NMR. (CCl_4): 1.0–1.3 (*m*, 6 H, all H_{ax}); 1.35 (*s*, 6 H, 2 H_3C(2)), 1.5–2.5 (*m*, 6 H, 4 H_{eq} and 2 H–C(7)); 3.0–3.4 (*m*, 5 H, 2 H–C(4), 2 (OH) and H–C(2′)); 6.55 (*m*, 2 H, CH = CH). – MS.: 212 (7), 197 (5), 179 (4), 161 (6), 154 (32), 136 (77), 121 (41), 111 (14), 107 (18), 94 (27), 82 (28), 81 (33), 67 (32), 59 (100), 41 (23).

$C_{14}H_{24}O_3$ (240.3) Calc. C 69.69 H 10.07% Found C 69.78 H 10.09%

(E)-*7-Hydroxy-7-methyl-1-phenyl-3-octen-1-one* (**14da**). Slightly yellow viscous oil (32%).

When the reaction was carried out in presence of HMPT, the yield of **14da** was improved to 38%. Rf 0.11 ether/pentane 2:3). – IR. (film): 3425, 3030, 1680, 1600, 1580, 1450, 1200, 970 (trans CH = CH), 925, 910, 750, 690. – ^{1}H-NMR. ($CDCl_3$): 1.12 and 1.16 (2*s*, 6 H, 2 H_3C–C(7)); 1.44 (*m*, 2 H, 2 H–C(6)); 2.08 (*m*, 2 H, 2 H–C(5)); 3.0 (br. *s*, 1 H, OH); 3.7 (*m*, 2 H, 2 H–C(2)); 5.65 (m, J (trans) = 16, 2 H, CH = CH); 7.2 and 8.0 (*m*, 5 H, aromat. H).

$C_{15}H_{20}O_2$ (232.3) Calc. C 77.54 H 8.62% Found C 76.68 H 8.71%

4. Cyclization of the hydroxyalkylated products *6* and *14* to THF-derivatives *7* and THP-derivatives *15*, respectively. – 4.1. *General procedure.* A solution of sodium methoxide (2.5 mmol) in methanol (15 ml) was added to the solution of hydroxyketone **6** or **14** (2.5 mmol) in THF (15 ml) and the reaction mixture was stirred at RT. for the period indicated in *Table 2*. The reaction mixture was then poured into water, acidified with 1N HCl and extracted with ether or pentane. The organic phase was washed three times with water and once with sat. NaCl-solution. It was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude products were obtained in almost quantitative yields. They were purified either by distillation or by chromatography over silicagel, using ether/pentane as solvent for elution. The ratios (see *Tables 1* and *2*) of the *cis*- and *trans*-diastereomers in the products were determined by capillary gas chromatography (0.125 *μ Pluronic L 64*, 20 m × 0.31 Glass) and ^{13}C-NMR. spectroscopy. The diastereomer ratio from ^{13}C-NMR. was taken as the ratio of the peak heights of signals (with respect to an appropriate peak, see the numbers given in parentheses). We are aware that these can only be approximate values; in many cases they agree well with ratios determined from ^{1}H-NMR. spectra (see for instance **7dc**) and from capillary GC.

4.2. *Data of the THF-derivatives* **7a, 7b, 7d**. – *1-(5-Phenyl-2-tetrahydrofuryl)-2-propanone* (**7aa**). The solvent for chromatography was ether/pentane 5:95, $n_D^{21} = 1.5200$. – IR. (film): 1715, 1605, 1490, 1450, 1360, 1065, 760, 705. – ^{1}H-NMR. (CCl_4): 1.66 (*m*, 2 H, 2 H–C(3′ or 4′)); 2.13 (*s*, 3 H, H_3C–C(2)); 2.2 (*m*, 2 H, 2 H–C(4′ or 3′)); 2.66 (*m*, 2 H, 2 H–C(1)); 4.33 (*m*, 1 H, H–C(2′ or 5′)); 4.83 (*m*, 1 H, H–C(5′ or 2′)); 7.23 (br. *s*, 5 H, aromat. H). – ^{13}C-NMR. ($CDCl_3$): 30.74, 31.57, 32.57, 34.18, 35.18, 35.11, 49.96, 75.75, 80.43 (27) and 81.02 (30) (C–O), 125.51, 125.80, 127.25, 128.35, 143.54, 206.98. – MS.: 204 (5), 144 (85), 120 (50), 105 (100), 77 (54), 43 (100).

$C_{13}H_{16}O_2$ (204.3) Calc. C 76.44 H 7.90% Found C 75.99 H 7.93%

1-(5-Methyl-5-phenyl-2-tetrahydrofuryl)-2-propanone (**7ac**). Purification by distillation, b.p. 90°/ 0.004 Torr, $n_D^{21} = 1.5117$. –^{1}H-NMR. (CCl_4): 1.43 (*s*, 3 H, H_3C–C(5′)); 1.6–2.3 (*m*, 4 H, 2 H–C(3′ and 4′)); 2.1 (*s*, 3 H, H_3C–C(1)); 2.46 (*d* × *d*, *J* = 16 and 6, 1 H, H–C(1)); 3.75 (2 *d* × *d*, *J* ≈ 16 and 6, 1 H, H–C(3)); 4.33 (*m*, 1 H, H–C(2′)); 7.23 (*m*, 5 H, aromat. H). –^{13}C-NMR. ($CDCl_3$): 29.87, 30.74, 30.97, 31.73, 31.93, 39.21, 39.72, 50.17, 50.40, 74.93, 75.18, 84.65 (16) and 84.79 (30) (C–O), 124.66, 126.42, 128.05, 128.25, 148.26, 206.93.

$C_{14}H_{18}O_2$ (218.3) Calc. 77.03 H 8.31% Found C 76.86 H 8.47%

1-(5,5-Diphenyl-2-tetrahydrofuryl)-2-propanone (**7ad**). The solvent for chromatography was ether/ pentane 1:9, m.p. 61–63° (from pentane). – IR. (film): 1715, 1600, 1490, 1450, 1360, 1230, 1180, 1055, 750, 705. –^{1}H-NMR. ($CDCl_3$): 1.66 (*m*, 1 H); 2.1 (*m*, 1 H); 2.16 (*s*, 3 H, H_3C–C(2)); 2.26–3.0 (*m*, 4 H, 2 H–C(3′ and 4′)); 4.43 (*qi*, *J* = 7, 1 H, H–C(2′)); 7.23 (*m*, 10 H, aromat. H). – MS.: 280 (1), 262 (19), 203 (74.5), 180 (76), 161 (59), 105 (100), 91 (11), 77 (41), 43 (62).

$C_{19}H_{20}O_2$ (280.4) Calc. C 81.39 H 7.14% Found C 81.36 H 7.29%

1-(5-Ethyl-2-tetrahydrofuryl)-3,3-dimethyl-2-butanone (**7ba**). Purification by distillation, b.p. 83°/2 Torr $n_D^{20.5} = 1.4426$. – IR. (film): 2970, 2880, 1705, 1480, 1465, 1370, 1220, 1200, 1050, 1000, 950, 880, 840, 760. –^{1}H-NMR. (CCl_4) (Diastereomeric mixture 44:56): 0.88 (*t*, *J* = 7, 3 H, CH_3CH_2); 1.1 (*s*, 9 H, 3 H_3C–C(3)); 1.2–1.6 (*m*, 4 H, 2 H–C(3′ and 4′)); 1.7–2.15 (*m*, 2 H); 2.35 (*d* × *d*, *J* = 16.5 and 6, 1 H, H–C(1)); 2.85 (*d* × *d*, *J* = 16.5 and 6, 1 H, H–C(1)); 3.2 (*m*, 1 H, H–C(2′ or 5′)); 4.15 (*m*, 1 H, H–C(5′ or 2′)). – ^{13}C-NMR. ($CDCl_3$): 10.28, 26.21, 28.75, 28.87, 30.58, 31.44, 31.53, 32.45, 42.91, 43.11, 44.19, 74.89, 80.14 (34) and 80.57 (30) (C–O), 214.14. – MS.: 198 (0.9), 142 (18.7), 141 (36.6), 99 (84,5), 85 (37.3), 81 (56), 57 (100), 41 (27.9), 29 (19.8).

$C_{12}H_{22}O_2$ (198.3) Calc. C 72.68 H 11.18% Found C 72.26 H 11.04%

1-(5-Isopropyl-2-tetrahydrofuryl)-3,3-dimethyl-2-butanone (**7bb**). Purification by distillation, b.p. 90°/1 Torr, $n_D^{20.5} = 1.4446$. – IR. (film): 2970, 1710, 1475, 1365, 1050, 1000, 610. – ^{1}H-NMR. (CCl_4) 0.83 and 0.9 (2*d*, *J* = 6, 6 H, 2 H_3C–CH); 1.1 (*s*, 9 H, 3 H_3C–C(3)); 1.2–2.2 (*m*, 5 H); 2.34 (*d* × *d*, *J* = 16.5 and 6, 1 H, H–C(4)); 2.85 (*d* × *d*, *J* = 16.5 and 6, 1 H, H–C(4)); 3.45 (*m*, 1 H, H–C(2′ or 5′)); 4.15 (*m*, 1 H, H–C(5′ or 2′)). – ^{13}C-NMR. ($CDCl_3$): 18.32, 18.43, 19.33, 26.19, 28.44, 29.60, 31.61, 32.76, 33.21, 42.94, 44.25, 75.44, 84.29 (22) and 84.66 (15) (C–O), 214.29. – MS.: 212 (0.5), 169 (11.3), 155 (14.7), 113 (17), 95 (42.4), 85 (52), 69 (15.9), 57 (100), 41 (22.8).

$C_{13}H_{24}O_2$ (212.3) Calc. C 73.58 H 11.32% Found C 73.39 H 11.47%

3,3-Dimethyl-1-(5-phenyl-2-tetrahydrofuryl)-2-butanone (**7bc**). Purification by distillation, b.p. 105°/0.002 Torr, $n_D^{21} = 1.5060$. – IR. (film): 3060, 3030, 2980, 2880, 1705, 1605, 1495, 1480, 1475, 1450, 1370, 1220, 1050, 1005, 940, 850, 760, 700. – ^{1}H-NMR. (CCl_4): 1.03 (*s*, 9 H, 3 H_3C–C(3)); 1.4–2.4 (*m*, 4 H, 2 H–C(3′ and 4′)); 2.5 (*d* × *d*, *J* = 16.5 and 6, 1 H, H–C(1)); 3.0 (*d* × *d*, *J* = 16.5 and 6, 1 H, H–C(1)); 4.4 (*m*, 1 H, H–C(2′ or 5′)); 4.86 (*m*, 1 H, H–C(5′ or 2′)), 7.23 (br. *s*, 5 H, aromat. H). – ^{13}C-NMR. ($CDCl_3$): 26.31, 31.70, 32.80, 34.25, 35.25, 42.90, 44.26, 76.14, 80.24 (10) and 80.68 (14) (C–O), 125.54, 125.81, 127.18, 128.31, 143.23, 213.72. – MS.: 246 (1.3), 189 (10.8), 147 (100), 142 (78.3), 129 (33.3), 120 (31.5), 118 (12.9), 107 (12.6), 105 (29.3), 104 (54.1), 91 (52.1), 85 (46.4), 78 (12), 77 (16.7), 57 (94.7), 41 (30.3).

$C_{16}H_{22}O_2$ (246.3) Calc. C 78.01 H 9.00 O 12.99% Found C 77.51 H 9.22 O 12.66%

3,3-Dimethyl-1-(1-oxaspiro[4.5]dec-2-yl)-2-butanone (**7bf**). The solvent used for chromatography was ether/pentane 5:95, b.p. 100°/0.01 Torr, $n_D^{20} = 1.4663$. – IR. (film): 2940, 2860, 1705, 1480, 1450, 1370, 1310, 1050, 1000, 950, 900, 770, 740. – ^{1}H-NMR. (CCl_4): 1.1 (*s*, 9 H, 3 H_3C–C(3)); 1.2–1.8 (br. *m*, 11 H); 2.1 (*m*, 1 H); 2.35 (*d* × *d*, *J* = 16.5 and 6, 1 H, H–C(1)); 2.85 (*d* × *d*, *J* = 16.5 and 6, 1 H, H–C(1)); 4.2 (*m*, 1 H, H–C(2′)). – MS.: 238 (3), 195 (17), 142 (40.5), 139 (22.7), 138 (24.5), 121 (28.5), 111 (11.6), 99 (6.1), 95 (15), 85 (74.9), 81 (13.3), 57 (100), 55 (26.7), 41 (26.5).

$C_{15}H_{26}O_2$ (238.4) Calc. C 75.58 H 11.00 O 13.42% Found C 75.44 H 11.00 O 13.61%

3,3-Dimethyl-1-(5,5-diphenyl-2-tetrahydrofuryl)-2-butanone (**7bj**). The solvent used for chromatography was ether/pentane 1:9, m.p. 46–47° (from ether/pentane 1:4). – IR. (CCl_4): 3090, 3060, 3030, 2980, 2910, 2880, 1900, 1880, 1800, 1700, 1600, 1490, 1480, 1460, 1450, 1370, 1300, 1230, 1050, 915, 890, 705. – ^{1}H-NMR. (CCl_4): 1.1 (*s*, 9 H, 3 H_3C–C(3)); 1.56 and 2.1 (*m*, 2 H, 2 H–C(3′)); 2.53 (*m*, 3 H); 3.3 (*d* × *d*, *J* = 16.5 and 6, 1 H, H–C(1)); 4.45 (*m*, 1 H, H–C(2′)); 6.93–7.5 (*m*, 10 H, aromat. H). – MS.: 322 (0.84), 304 (9.3), 245 (19.5), 223 (20.3), 205 (19.7), 204 (16.1), 183 (20.9), 180 (100), 165 (14.3), 142 (18.4), 115 (11.4), 105 (60.6), 91 (10.4), 85 (23.5), 77 (14.7), 57 (63.3), 41 (10.7).

$C_{22}H_{26}O_2$ (322.4) Calc. C 81.89 H 8.07 O 9.92% Found C 81.80 H 8.21 O10.03%

1-Phenyl-2-(5-ethyl-2-tetrahydrofuryl)-1-ethanone (**7da**). The solvent used for chromatography was ether/pentane 5:95. It is obtained as slightly yellow oil, $n_D^{22} = 1.5206$. – IR. (film): 3030, 2950, 1680, 1600, 1580, 1445, 1370, 1270, 1200, 1070, 880, 750, 690. – ^{1}H-NMR. (CCl_4) (Diastereomeric mixture 1:1): 0.95 (*t*, *J*=6.5, 3 H, CH_3CH_2); 1.48 (*m*, 4 H); 2.08 (*m*, 2 H); 2.9 (*d*×*d*, *J*=7 and 16, 1 H, H–C(2)); 3.35 (*m*, 1 H, H–C(2)); 3.66 (*m*, 1 H, H–C(2′ or 5′)); 4.28 (*m*, 1 H, H–C(5′ or 2′)); 7.48 and 7.96 (*m*, 5 H, aromat. H). ^{13}C-NMR. ($CDCl_3$): =10.26, 28.75, 28.86, 30.53, 31.45, 32.37, 45.12, 45.28, 75.01, 75.86, 80.37 (22) and 80.85 (23) (C–O), 128.28, 128.55, 129.09, 133.05. – MS.: 218 (1), 212 (21), 105 (100), 77 (45), 43 (18).

$C_{14}H_{18}O_2$ (218.4) Calc. C 77.07 H 8.25% Found C 77.36 H 8.03%

ω-(5-Isopropyl-2-tetrahydrofuryl)acetophenone (**7db**). The solvent used for chromatography was ether/pentane 1:9. Faint yellow oil, $n_D^{21} = 1.5168$. – IR. (film): 2960, 1680, 1590, 1580, 1480, 1445, 1200, 1060, 1000, 750, 690. – ^{1}H-NMR. (CCl_4): 0.86 and 0.9 (2*d*, *J*=6, 6 H, 2 H_3C–CH); 1.23–2.24 (*m*, 5 H); 2.88 (*d*×*d*, *J*=7 and 16, 1 H, H–C(2)); 3.35 (*m*, 1 H, H–C(2)); 3.5 (*m*, 1 H, H–C(2′ or 5′)); 4.3 (*m*, 1 H, H–C(2′ or 5′)); 7.45 and 7.95 (*m*, 5 H, aromat. H). – ^{13}C-NMR. ($CDCl_3$): 18.37, 19.26, 28.33, 29.46, 31.60, 32.48, 32.71, 33.18, 45.11, 75.48, 84.41 (24) and 84.88 (28) (C–O), 128.29, 128.53, 128.90, 129.25, 132.99.

$C_{15}H_{20}O_2$ (232.3) Calc. C 77.54 H 8.62% Found C 77.00 H 8.75%

ω-(5-Phenyl-2-tetrahydrofuryl)acetophenone (**7dc**). Yellowish crystals, m.p. 91–95°. – IR. (KBr): 3060, 3020, 2960, 2860, 1680, 1590, 1580, 1490, 1450, 1210, 1180, 1055, 750, 700. – ^{1}H-NMR. (CCl_4) (Diastereomeric mixture 39:61): 1.66 (*m*, 2 H, 2 H–C(3′ or 4′)); 2.24 (*m*, 2 H, 2 H–C(4′ or 3′)); 2.98 and 3.44 (2*m*, 2 H, 2 H–C(2)); 7.26 (br. *s*, 5 H, aromat. H); 7.44 and 7.96 (*m*, 5 H, aromat. H). – ^{13}C-NMR. ($CDCl_3$): 31.68, 32.64, 34.22, 35.19, 44.98, 76.16, 80.42 (14) and 80.91 (20) (C–O), 125.58, 125.83, 127.23, 127.85, 128.29, 128.64, 129.11, 129.46, 133.15.

$C_{18}H_{18}O_2$ (266.3) Calc. C 81.20 H 6.81% Found C 81.55 H 6.72%

ω-(1-Oxaspiro-[4.5]dec-2-yl)acetophenone (**7dd**). Slightly yellow oil after chromatography with ether/pentane 5:95 as solvent, $n_D^{25} = 1.5342$. – IR. (film): 2920, 2850, 1680, 1590, 1580, 1445, 1205, 1065, 750, 685. – ^{1}H-NMR. (CCl_4): 1.06–1.9 (br. *m*, 13 H); 2.15 (*m*, 1 H); 2.85 and 3.32 (2*d*×*d*, *J*=7 and 16.5, 2 H, 2 H–C(2)); 4.36 (*m*, 1 H, H–C(2′)); 7.44 and 7.94 (*m*, 5 H, aromat. H).

$C_{17}H_{22}O_2$ (258.4) Calc. C 79.07 H 8.52% Found C 79.08 H 8.50%

ω-[5-(3-Butenyl)-5-phenyl-2-tetrahydrofuryl]acetophenone (**7de**). The solvent used for chromatography was ether/pentane 5:95 $n_D^{22} = 1.5573$. – IR. (film): 3050, 2940, 1680, 1640, 1600, 1580, 1490, 1445, 1205, 1050, 910, 750, 700. – ^{1}H-NMR. (CCl_4) (Diastereomeric mixture 62:38): 1.0–2.4 (*m*, 8 H, methylene H); 2.98 (*d*×*d*, *J*=7 and 16, 1 H, H–C(2)); 3.44 (*d*×*d*, *J*=7 and 16, 1 H, H–C(2)); 4.9 (*m*, 1 H, H–C(2′)); 4.88 (*m*, 2 H, CH_2=C); 5.68 (*m*, 1 H, CH=C); 7.2, 7.4 and 7.96 (*m*, 10 H, aromat. H). – ^{13}C-NMR. ($CDCl_3$): 28.70, 31.72, 38.03, 38.69, 41.63, 42.67, 45.10, 75.08 (30) and 75.79 (18) (C–O), 86.79.

$C_{22}H_{22}O_2$ (318.4) Calc. C 82.50 H 7.50% Found C 82.48 H 7.65%

ω-(5,5-Diphenyl-2-tetrahydrofuryl)acetophenone (**7df**). The solvent used for chromatography was ether/pentane 1:9, m.p. 84–85° (ether/pentane 1:1). – IR. (KI): 3030, 3010, 1675, 1595, 1490, 1450, 1380, 1200, 1050, 1020, 750, 700. – ^{1}H-NMR. ($CDCl_3$): 1.8 (*m*, 1 H); 2.22 (*m*, 1 H); 2.6 (*m*, 2 H); 3.02 and 3.48 (*d*×*d*, *J*=7 and 16, 2 H, 2 H–C(2)); 4.66 (*m*, 1 H, H–C(2′)); 7.26 and 7.88 (*m*, 15 H, aromat. H).

$C_{24}H_{22}O_2$ (342.4) Calc. C 84.18 H 6.47% Found C 83.95 H 6.37%

4.2. *Data of the THP-derivatives* **15a–d**. – *1-(6,6-Dimethyl-2-tetrahydropyranyl)-2-propanone* (**15aa**). Purification by chromatography with ether/pentane 3:7 as solvent, $n_D^{21.5} = 1.4443$. – IR. (film): 2980, 2940, 1720, 1370, 1290, 1220, 1170, 1080, 1060, 1050, 1010, 980, 900. – ^{1}H-NMR. (CCl_4): 0.7–1.85 (*m*, 6 H, methylene H); 1.12 and 1.16 (2*s*, 6 H, 2 H_3C–C(6′)); 2.06 (*s*, 3 H, H_3C–C(2)); 2.33 (*m*, 2 H, 2 H–C(1)); 3.9 (*m*, 1 H, H–C(2′)). – MS.: 170 (2), 152 (7), 113 (16), 100 (27), 69 (14), 56 (28), 43 (100).

$C_{10}H_{18}O_2$ (170.2) Calc. C 70.54 H 10.66% Found C 70.61 H 10.57%

1-(6-Phenyl-2-tetrahydropyranyl)-2-propanone (**15ab**) *and 1-(5-phenyl-2-tetrahydropyranyl)-2-propanone* (**15ac**). A mixture of **14ab** and **14ac** was treated with sodium methoxide to furnish **15ab** (23%) and **15ac** (15%) after chromatography over silicagel, using ether/pentane 3:7 as solvent for elution.

Data of **15ab**. Oil, $n_D^{20.5} = 1.5212$. – IR. (film): 2940, 1715, 1605, 1490, 1450, 1360, 1200, 1085, 1045, 920, 750. – ^{1}H-NMR. (CCl_4): 1.0–2.03 (*m*, 6 H, methylene H); 2.16 (*s*, 3 H, H_3C–C(2)); 2.5 (*d*×*d*, *J*=6

and 16, 1 H, H–C(1)); 2.8 ($d \times d$, J=7 and 16, 1 H, H–C(1)); 4.0 (*m*, 1 H, H–C(2′)); 4.4 ($d \times d$, J=2.5, $J_{ax,ax}$=10, 1 H, H–C(6′)); 7.2 (*m*, 5 H, aromat. H). – MS.: 218 (3), 200 (28), 160 (30), 107 (62), 91 (25), 77 (29), 43 (100).

$C_{14}H_{28}O_2$ (218.3) Calc. C 77.03 H 8.31% Found C 76.94 H 8.34%

Data of **15ac**. Oil, $n_D^{21.5}$ = 1.5170. – IR. (film): 2940, 2860, 1710, 1600, 1490, 1450, 1360, 1160, 1110, 1085, 900, 760, 705. – ^{1}H-NMR. (CCl_4): 1.1–2.13 (*m*, 4 H, CH_2CH_2); 2.1 (*s*, 3 H, H_3C–C(2)); 2.33 ($d \times d$, J=5 and 16, 1 H, H–C(1)); 2.76 (*m*, 1 H, H–C(5′)); 3.36 (*t*, J=11, 1 H); 3.73 (*m*, 2 H); 7.16 (m, 5 H, aromat. H). – MS.: 218 (2), 200 (4), 142 (27), 118 (29), 104 (100), 91 (41), 43 (39).

$C_{14}H_{18}O_2$ (218.3) Calc. C 77.03 H 8.31% Found C 76.80 H 8.21%

(±)-3,3-Dimethyl-1-(6-methyl-2-tetrahydropyranyl)-2-butanone (**15ba**). Purification by distillation, b.p. 56°/1 Torr, n_D^{24} = 1.4448. – IR. (film): 2980, 2940, 2725, 1710, 1480, 1460, 1370, 1340, 1205, 1090, 1070, 1045, 1020, 990, 890. – ^{1}H-NMR. (CCl_4): 1.03 (*d*, J=6, 3 H, CH_3C); 1.06 (*s*, 9 H, 3 H_3C–C(3)); 1.2–2.8 (*m*, 6 H, methylene H); 2.03–2.85 (*m*, 2 H, 2 H–C(1)); 3.36, 3.73 and 4.1 (*m*, 2 H, 2 H–C(2′ and 6′)). – ^{13}C-NMR. ($CDCl_3$): 18.34, 19.10, 22.16, 23.55, 26.14, 30.14, 31.16, 33.20, 41.13, 43.64, 44.26, 67.07, 67.93, 73.96 (22) and 74.21 (33) (C–O), 213.96. – MS.: 198 (1.5), 180 (1), 141 (36.4), 99 (100), 85 (10.5), 81 (55.5), 57 (49.5), 55 (15.8), 43 (13.4), 41 (19.1).

$C_{12}H_{22}O_2$ (198.3) Calc. C 72.68 H 11.18 O 16.17% Found C 72.57 H 11.19 O 16.30%

After stirring for 96 h, 0.5 g (100%) of the more stable isomer was isolated. – IR. (film): 2960, 2930, 2860, 1710, 1480, 1460, 1440, 1390, 1370, 1340, 1320, 1205, 1160, 1080, 1040, 990, 960, 890, 840, 760. – ^{1}H-NMR. (CCl_4): 1.06 (*s*, 9 H, 3 H_3C–C(3)); 1.03 (*d*, J=6, 3 H, H_3C–C(6′)); 0.8–1.85 (*m*, 6 H, methylene H); 2.23 and 2.7 ($2d \times d$, J=16.5 and 6, 2 H, 2 H–C(1)); 3.36 (*m*, 1 H, H–C(2′ or 6′)); 3.75 (*m*, 1 H, H–C(6′ or 2′).

(+)-(S,S)-(**15ba**). Yield 100% (crude product, n_D^{21} = 1.4454), $[\alpha]_D^{21}$ = +37.79° (*c*=2.04, benzene).

3,3-Dimethyl-1-(6,6-dimethyl-2-tetrahydropyranyl)-2-butanone (**15bb**). Purification by distillation b.p. 80°/5 Torr, n_D^{23} = 1.4435. – IR. (film): 2980, 2940, 2880, 1710, 1480, 1380, 1370, 1280, 1220, 1090, 1080, 1045, 980, 880, 830. – ^{1}H-NMR. (CCl_4): 1.1 (*s*, 12 H, 3 H_3C–C(3) and H_3C(6′)); 1.15 (*s*, 3 H, H_3C–C(6′)); 1.2–1.85 (*m*, 6 H, methylene H); 2.18 ($d \times d$, J=16 and 6, 1 H, H–C(1)); 2.65 ($d \times d$, J=16 and 6, 1 H, H–C(1)); 3.95 (*m*, 1 H, H–C(2′)). – MS.: 212 (4.9), 194 (3.8), 155 (30), 142 (18.1), 137 (13.8), 113 (49.3), 97 (14), 95 (67.2), 85 (32.2), 57 (100), 41 (30.7).

$C_{13}H_{24}O_2$ (212.3) Calc. C 73.53 H 11.39% Found C 73.16 H 11.33%

3,3-Dimethyl-1-(2-hexahydrochromanyl)-2-butanone (**15bc**). Purification by distillation, b.p. 110°/0.02 Torr, n_D^{20} = 1.4712. – IR. (film): 2930, 2860, 1710, 1480, 1450, 1365, 1235, 1115, 1080, 1060, 990, 960, 880, 760. – ^{1}H-NMR. (CCl_4): 1.06 (*s*, 9 H, 3 H_3C–C(3)); 0.9–1.9 *(m)*; 2.2 ($d \times d$, J=16 and 6, 1 H); 2.63–3.03 *(m)*; 3.7 *(m)*; 4.3 *(m)*. – MS.: 238 (4), 220 (3), 181 (40.8), 139 (78.5), 121 (100), 95 (10), 57 (25), 41 (12).

$C_{15}H_{26}O_2$ (238.4) Calc. C 75.58 H 11.00 O 13.42% Found C 75.39 H 10.97 O 13.91%

After stirring for 70 h, the more stable isomer was isolated. – ^{1}H-NMR. (CCl_4): 1.06 (*s*, 9 H, H_3C–C(3)); 0.7–1.9 (br. *m*, 13 H); 2.2 ($d \times d$, J=16.5 and 6, 1 H, H–C(1)); 2.23 ($d \times d$, J=16.5 and 6, 1 H, H–C(1)); 2.9 (*m*, 1 H, H–C(2′ or 9′)); 3.2 (*m*, 1 H, H–C(9′ or 2′)).

*(±)-3-Hydroxy-3-methyl-1-(*cis*-6-methyl-2-tetrahydropyranyl)-2-butanone* (**15ca**). The compound **15ca** was obtained in pure form after usual workup of the reaction mixture (yield 98%). – IR. (film): 3450, 2970, 2930, 2855, 1710, 1440, 1370, 1335, 1280, 1265, 1205, 1180, 1150, 1080, 1030, 1000, 965, 900, 850, 795, 765. – ^{1}H-NMR. (CCl_4): 1.12 (*d*, J=7, 3 H, H_3C–C(6′)); 1.3 (*s*, 6 H, 2 H_3C–C(3)); 1.4–2.0 (*m*, 6 H, $-(CH_2)_3-$); 2.35 ($d \times d$, J=14 and 5, 1 H, H–C(1)); 2.85 ($d \times d$, J=14 and 8, 1 H, H–C(1)); 3.3–4.9 (*m*, 3 H, H–C(2′) and OH).

$C_{11}H_{20}O_3$ (200.3) Calc. C 65.97 H 10.07% Found C 65.77 H 10.20%

(+)-(S,S)-*3-Hydroxy-3-methyl-1-(*cis*-6-methyl-2-tetrahydropyranyl)-2-butanone* (**15ca**). To a solution of sodium methoxide (20 mmol) in methanol (10 ml) and THF (20 ml) was added a solution of (+)-*(S)*-**14ca** (2 g, 10 mmol) in THF (10 ml). The reaction mixture was stirred at RT. for 2 h. Workup, as described in the general procedure, furnished **15ca** as colorless oil (1.78 g, 89%), n_D^{22} = 1.4967, $[\alpha]_D^{20}$ = +34.12 (*c*=2.0, $CHCl_3$). – IR. spectrum was identical with authentic (±)-**15ca**, described above. – ^{1}H-NMR. ($CDCl_3$): 1.13 (*d*, J=6, 3 H, H_3C–C(6′)); 1.33 (*s*, 6 H, 2 H_3C–C(3)); 1.7 (br. *m*, 6 H, methylene H); 2.47 ($d \times d$,

J=15 and 4.5, 1 H, H–C(1)); 3.0 ($d\times d$, J=15 and 7.5, 1 H, H–C(1)); 3.46 (*m*, 1 H, H–C(2')); 3.8 (*m*, 1 H, H–C(6')); 4.26 (*s*, 1 H, exchanges with D_2O, OH).

1-(2-Hexahydrochromanyl)-3-hydroxy-3-methyl-2-butanone (**15cc**). Purification by distillation, b.p. 90°/0.001 Torr. – IR. (film): 3450, 2970, 2920, 2850, 1708, 1450, 1370, 1350, 1275, 1195, 1110, 1080, 1050, 990, 965, 950, 860. – ^{1}H-NMR. (CCl_4): 1.0–2.0 (*m*, 14 H, methylene H and H–C(10')); 1.25 (*s*, 6 H, 2 H_3C–C(3)); 2.33 ($d\times d$, J=14 and 5, H–C(1)); 2.87 ($d\times d$, J=14 and 8, H–C(1)); 3.5–3.9 (*m*, 3 H, H–C(2' and 9') and OH). – MS.: 241 (2), 212 (16), 197 (5), 154 (74), 139 (21), 136 (73), 121 (47), 111 (42), 107 (15), 98 (26), 95 (29), 82 (24), 81 (25), 67 (30), 59 (100), 41 (23), 31 (10).

$C_{14}H_{24}O_3$ (240.3) Calc. C 69.96 H 10.07% Found C 70.13 H 9.99%

ω-(6,6-Dimethyl-2-tetrahydropyranyl)acetophenone (**15da**). The solvent used for chromatography was ether/pentane 1:9, n_D^{21} = 1.5196. – IR. (film): 2980, 2920, 1680, 1600, 1580, 1450, 1375, 1360, 1280, 1200, 1060, 975, 750, 690. – ^{1}H-NMR. (CCl_4): 1.1 and 1.16 (2*s*, 6 H, 2 H_3C–C(6')); 1.36–1.64 (*m*, 6 H, methylene H); 2.72 and 3.14 ($d\times d$, J=16 and 7, 2 H, 2 H–C(2)); 4.12 (*m*, 1 H, H–C(2')); 7.44 and 7.92 (*m*, 5 H, aromat. H).

$C_{15}H_{20}O_2$ (232.3) Calc. C 77.59 H 8.62% Found C 77.59 H 8.65%

5. *Baeyer-Villiger* oxidation of the phenyl derivative *8bj*. – *Preparation of (5,5-diphenyl-2-tetrahydrofuryl)acetic acid* (**16a**). To a solution of **7bj** (0.32 g, 1 mmol) in acetic acid (5 ml) was added 30% H_2O_2- or 70% H_2O_2-solution in excess. The reaction mixture was kept at 50–60° for 120 h or 40–50° for 96 h. It was poured into water and extracted with ether. Usual workup gave **16a**, which was directly converted to the methyl ester **16b** *(methyl (5,5-diphenyl-2-tetrahydrofuryl)acetate)*.

The crude product **16a** was dissolved in absolute methanol. Sulfuric acid (conc., 3 drops) was added and the reaction mixture was refluxed for 4 h. The crude product obtained was purified by preparative layer chromatography (silicagel *PF254*, ether/pentane 1:5) to furnish the methylester **16b** (0.07 g, 26%), m.p. 54–55° (from ether/pentane 1:9). – IR. (film): 3065, 3025, 2960, 1740, 1600, 1490, 1450, 1440, 1380, 1300, 1200, 1175, 1055, 920, 893, 705. – ^{1}H-NMR. (CCl_4): 1.73 (*m*, 1 H); 2.1 (*m*, 1 H); 2.56 (*m*, 4 H); 3.63 (*s*, 3 H, CH_3O); 4.46 (*qi*, 1 H, CHO); 7.26 (*m*, 10 H, aromat. H).

$C_{19}H_{20}O_3$ (296.3) Calc. C 77.00 H 6.80% Found C 76.99 H 6.85%

6. Conversion of the ketones *7* and *15* to carboxylic acids *via Beckmann* rearrangement. – The oximes prepared by usual methods [14] were treated with PCl_5 in absolute ether and the products obtained were hydrolyzed with aq. KOH-solution to give the acids.

6.1. *Synthesis of (5,5-diphenyl-2-tetrahydrofuryl)acetic acid* (**16a**). – *Preparation of 3,3-dimethyl-1-(5,5-diphenyl-2-tetrahydrofuryl)-2-butanone oxime (oxime of* **7bj**). M.p. 168–169° (from ethyl acetate). – IR. (CCl_4): 3250, 1600, 1490, 1450, 1050, 705. – ^{1}H-NMR. ($CDCl_3$): 1.16 (*s*, 9 H, 3 H_3C–C(3)); 1,9 (*m*, 2 H); 2.63 (*m*, 4 H); 4.5 (*m*, 1 H, H–C(2')); 7,26 (*m*, 10 H, aromat. H), 7.9 (br. *s*, 1 H, OH).

$C_{22}H_{27}NO_2$ (337.4) Calc. C 78.30 H 8.07% N 4.15% Found C 78.46 H 8.16 N 4.12%

Preparation of N-*(t-butyl)-2-(5,5-diphenyl-2-tetrahydrofuryl)acetamide* (**17**) *and (5,5-diphenyl-2-tetrahydrofuryl)acetonitrile* (**18**). To a suspension of PCl_5 (1.1 mmol) in absolute ether (15 ml) was added at 0° the oxime of **7bj** (1 mmol) in ether (5 ml). It was stirred over night (0° to RT.), poured into water and extracted with ether. The crude product obtained was purified by preparative layer chromatography (silicagel *PF254*, ethyl acetate/pentane 4:6) to furnish **17** (0.09 g, 26%) as crystalline compound, m.p. 114–115°, and **18** (0.18 g, 69%) as an oil.

Spectral data of **17.** – IR. (CCl_4): 3400, 2960, 1675, 1600, 1510, 1450, 1365, 1230, 1050, 700. – ^{1}H-NMR. ($CDCl_3$): 1.3 (*s*, 9 H, 3 H_3C–C–N); 1.6–2.93 (*m*, 6 H, 2 H–C(2,3' and 4')); 4.45 (*qi*, J=6, H–C(2')); 6.3 (br. *s*, 1 H, NH); 7.35 (*m*, 10 H, aromat. H). – MS.: 337 (0.4), 260 (20), 204 (15), 180 (20), 157 (100), 149 (25), 105 (45.6), 57 (40.5).

$C_{22}H_{27}ON$ (337.4) Calc. C 78.30 H 8.07 N 4.15 Found C 78.21 H 8.02 N 4.08

Spectral data of **18.** – IR. (film): 2250, 1600, 1390, 1450, 1230, 1060, 760, 705. – ^{1}H-NMR. (CCl_4): 1.5–2.85 (*m*, 6 H, CH_2CN, CH_2CH_2); 7.25 (*m*, 10 H, aromat. H).

Preparation of (5,5-diphenyl-2-tetrahydrofuryl)acetic acid (**16a**). The crude product containing **17** and **18** (0.4 g) was treated with 50% aq. KOH-solution (5 ml) in ethylene glycol (10 ml) and heated at 150° for 6 to 8 h. After neutralization with dil. HCl three extractions with ethyl acetate and the usual workup gave the acid **16a** (0.23 g, 81.5%), m.p. 138–139° (from ethyl acetate). – IR. ($CHCl_3$): 2500–3200, 1715,

1600, 1490, 1450, 1050, 700. – ^{1}H-NMR. ($CDCl_3$): 1.8 and 2.16 (*m*, 2 H); 2.66 (*m*, 4 H); 4.55 (*qi*, *J*=7, 1 H, H–C(2')); 7.3 (*m*, 10 H, aromat. H). – MS.: 282 (28), 205 (100), 196 (35), 149 (25), 105 (83), 77 (27), 43 (55).

The methyl ester **16b** was obtained in 64% yield as described above. M.p. 54–55°, the substance was identical in every respect with that obtained from the *Baeyer-Villiger* reaction above.

6.2. *Synthesis of methyl-(5-phenyl-2-tetrahydrofuryl)acetate* (**19**). – *Preparation of 3,3-dimethyl-1-(5-phenyl-2-tetrahydrofuryl)-2-butanone oxime* (*oxime of* **7bc**). Obtained from 2.35 g of **7bc**, in 76% yield (1.98 g) after filtration through silicagel, m.p. of the diastereomeric mixture 83–88°. – IR. (CCl_4): 3250, 1700, 1460, 1360, 1250, 1050, 940, 865, 700. – ^{1}H-NMR. (CCl_4) (Diastereomeric mixture): 1.2 (*s*, 9 H, *t*-C_4H_9); 1.5–2.0 (*m*, 2 H); 2.0–3.0 (*m*, 4 H); 4.2–5.03 (*m*, 2 H, 2 (CHO)); 7.2 (*m*, 5 H, aromat. H), 9.25 (br. *s*, 1 H, OH).

After crystallization of 1 g of the oxime from pentane/ether 7:3, 0.12 g of a 90% diastereomerically pure sample, m.p. 104–106°, was isolated, which, on further crystallization from the solvent mixture, furnished 42 mg of pure material of m.p. 109–110°, the configuration of which could not be assigned. – IR. (CCl_4): 3260, 3015, 2980, 2900, 2860, 1650, 1600, 1490, 1460, 1390, 1365, 1215, 1160, 1125, 1080, 1050, 1030, 940, 880. – ^{1}H-NMR. ($CDCl_3$): 1.16 (*s*, 9 H, 3 H_3C–C(3)); 1.8 (*m*, 2 H, CH_2); 2.3 (*m*, 2 H, CH_2); 2.56 and 2.76 (*d*×*d*, *J*=14 and 6, 2 H, 2 H–C(1)); 4.7 (*qi*, *J*=6, 1 H, H–C(2' or 5')); 5.03 (*t*, *J*=6, 1 H, H–C(5' or 2')); 7.3 (*m*, 5 H, aromat. H); 9.0 (*s*, 1 H, OH). – ^{13}C-NMR. ($CDCl_3$): 28.24, 32.52, 32.98, 35.10, 37.46, 77.29, 80.02, 125.54, 127.01, 128.26, 143.92, 165.03.

$C_{16}H_{23}O_2N$ (261.3) Calc C. 73.53 H 8.87 N 5.36% Found C 73.47 H 8.96 N 5.26%

Preparation of methyl (5-phenyl-2-tetrahydrofuryl)acetate (**19**). The oxime of **7bc** (1 g, 4 mmol) on reaction with PCl_5 (0.94 g, 4.5 ml) in absolute ether (20 ml) gave a nitrile, following the same procedure as in case of **17** and **18**. The nitrile was hydrolyzed using aq. KOH-solution (50%, 20 ml) in ethylene glycol (20 ml). The reaction mixture was heated at 150° for 10 h, to furnish the acid, after usual workup. This acid was esterified using the same procedure as for **16b**. The methyl ester **19** (0.35 g, 40%) was obtained after chromatographic filtration over silicagel (20 g, ether/pentane 5:95); n_D^{21} = 1.5142. – IR. (film): 3030, 2960, 2880, 1740, 1605, 1495, 1440, 1280, 1200, 1150, 1060, 760, 700. – ^{1}H-NMR. (CCl_4) (Diastereomeric mixture): 1.75 (*m*, 2 H, 2 H–C(3' or 4')); 2.25 (*m*, 2 H, 2 H–C(3' or 4')); 2.56 (*m*, 2 H, 2 H–C(2)); 3.63 (*s*, 3 H, OCH_3); 4.36 and 4.83 (*m*, 2 H, H–C(2')); 7.3 (*m*, 5 H, aromat. H). – MS.: 220 (18), 147 (31), 120 (100), 105 (47), 91 (37.5), 77 (25), 55 (21).

$C_{13}H_{16}O_3$ (220.3) Calc. C 70.89 H 7.32% Found C 70.80 H 7.38%

6.3. *Synthesis of the civet component. – 3,3-Dimethyl-1-(6-methyl-2-tetrahydropyranyl)-2-butanone oxime, oxime of* **15ba**, was not isolated in pure form and the crude product as such was used for the subsequent rearrangement.

*Preparation of (±)-*cis*-(6-methyl-2-tetrahydropyranyl)acetonitrile* (**20**). The oxime of **15ba** (0.77 g, 3 mmol) on reaction with PCl_5 (0.8 g, 3.8 mmol) in abs. ether (20 ml) gave the nitrile **20** (0.3 g, 69%), which was purified by passing it through silicagel (10 g column) and eluting with ether/pentane 5:95, b.p. 80°/1 Torr, n_D^{21} = 1.4493. – IR. (film): 2980, 2940, 2860, 2250, 1450, 1415, 1390, 1375, 1330, 1320, 1210, 1150, 1090, 1060, 1000, 970, 930, 900, 850. – ^{1}H-NMR. (CCl_4): 1.13 (*d*, *J*=7, 3 H, H_3C–C(6')); 1.63 (*m*, 6 H, methylene H); 2.4 (*m*, 2 H, 2 H–C(2)); 3.5 (*m*, 2 H, H–C(2' and 6')). – MS.: 139 (8), 124 (60), 99 (100), 81 (76), 68 (72), 55 (100), 41 (61).

$C_8H_{13}NO$ (139.2) Calc. C 69.03 H 9.41 N 10.06% Found C 68.88 H 9.49 N 9.44%

*(+)-(*S,S*)-***20***:* crude product, n_D^{21} = 1.4495, $[\alpha]_D^{21}$ = –1.75 (*c* = 1.375, benzene).

*Preparation of (±)-*cis*-(6-methyl-2-tetrahydropyranyl)acetic acid* (**22a**). The nitrile **20** (4.17 g, 30 mmol) on reaction with aq. KOH-solution (50%, 60 ml) in ethylene glycol (70 ml) gave the acid **22a** (3.74 g, 63%) after distillation of the crude product; b.p. 150°/0.004 Torr, m.p. 50–52° (from pentane) (m.p. [15] 52–53°). – The spectral data were in agreement with the values reported for the (±)-synthetic product [15] [17].

*Data of (±)-*cis*-methyl (6-methyl-2-tetrahydropyranyl)acetate* (**22b**). B.p. 70°/0.6 Torr b.p. [15]: 92°/10 Torr (bath temperature), n_D^{20} = 1.4402. – IR. (film): 2970, 2930, 2830, 1740, 1435, 1370, 1340, 1285, 1250, 1200, 1170, 1070, 1040, 1000, 910, 850. – ^{1}H-NMR. (CCl_4): 1.1 (*d*, *J*=7, 3 H, H_3C–C(6')); 0.86–2.0 (*m*, 6 H, methylene H); 2.23 and 2.46 (*d*×*d*, *J*=15 and 6, 2 H, 2 H–C(2)); 3.2–3.83 (*m*, 2 H, H–C(2' and 6')); 3.6 (*s*, 3 H, CH_3O).

$C_9H_{16}O_3$ (172.2) Calc. C 62.76 H 9.36% Found C 62.70 H 9.26%

*Data of (+)-*cis*-(S,S)-(6-methyl-2-tetrahydropyranyl)acetic acid* (**22a**). Obtained from THP-ketone **15ba** in 50% yield, b.p. 150°/0.004 Torr; viscous liquid, $[\alpha]_D^{22} = +32.86°$ ($c = 1.05$, benzene). – The spectral data were in agreement with the values reported for the (±)-synthetic product [15] [17].

(+)-(S,S)-(**22b**): B.p. 70°/0.6 Torr; $n_D^{20} = 1.4402$, $[\alpha]_D^{21} = +31.97°$ ($c = 1.2$, benzene). – The spectral data was in agreement with the values reported for the methyl ester of the natural product [15] [17].

6.4. *Synthesis of (2-hexahydrochromanyl)acetonitrile* (**21a**). The crude product (0.69 g) obtained by reacting 0.76 g (3 mmol) of the oxime of **15bc** (m.p. 126–127°, ether/pentane 2:3) with PCl_5 (0.69 g, 3.3 mmol) in abs. ether (10 ml), on chromatography over silicagel (15 g, ether/pentane 1:9) furnished the nitrile **21a** (0.43 g, 80%) as colorless oil, b.p. 100°/0.004 Torr, $n_D^{21} = 1.4820$. – IR. (film): 2940, 2860, 2260, 1455, 1415, 1380, 1350, 1340, 1315, 1290, 1260, 1235, 1200, 1110, 1050, 1000, 960, 930, 890, 860, 840, 780, 700. – ^{1}H-NMR. (CCl_4): 0.7–2.06 (br. *m*, 13 H); 2.43 (*m*, 2 H, 2 H–C(2)); 3.56 (*m*, 2 H, H–C(2′ and 8a′)). – MS.: 179 (26), 136 (100), 121 (100), 95 (28), 81 (31), 67 (54), 41 (48).

$C_{11}H_{17}NO$ (179.2) Calc. C 73.70 H 9.56 N 7.81% Found C 73.52 H 9.61 N 7.69%

7. Conversion of *14ca, 14cc, 15ca* and *15cc* to the corresponding acids by periodic acid. – *Preparation of (±)-7-hydroxy-3-octenoic acid* (**23**). To a solution of **14ca** (2 g, 10 mmol) in water (20 ml) at 0° was added a solution of periodic acid (3 g, 13 mmol) in water (10 ml). It was stirred at RT. for ½ h and poured into a mixture of sat. salt solution (50 ml) and ether (200 ml). After separation of the organic phase, it was washed with sat. NaCl-solution, containing 10% sodiumthiosulfate and then with sat. salt solution. It was dried over $MgSO_4$ and the solvent was removed under reduced pressure to furnish **23** (1.58 g, 100%). – IR. (film): 3350, 3020, 2960, 2920, 1710, 1400, 1370, 1290, 1195, 1125, 1080, 970, 930, 895, 840. – ^{1}H-NMR. ($CDCl_3$): 1.2 (*d*, $J = 7$, 3 H, H_3C–C(7)); 1.5 (*qa*, $J = 7$, 2 H, 2 H–C(6)); 2.15 (*m*, 2 H, 2 H–C(5)); 3.1 (*m*, 2 H, 2 H–C(2)); 3.8 (*sext.*, $J = 7$, 1 H, H–C(7)); 5.6 (*m*, 2 H, CH=CH); 6.45 (br. *s*, 2 H, 2 OH).

Spectral data of the methyl ester of **23** (colorless oil). – IR. (film): 3420, 3020, 2965, 2925, 1735, 1435, 1400, 1370, 1330, 1255, 1195, 1165, 1130, 1085, 1015, 965, 930, 900, 845, 755. – ^{1}H-NMR. ($CDCl_3$): 1.2 (*d*, $J = 7$, 3 H, H_3C–C(7)); 1.5 (*qa*, $J = 7$, 2 H, 2 H–C(6)); 1.7 (br. *s*, 1 H, OH); 2.15 (*m*, 2 H, 2 H–C(5)); 3.1 (*m*, 2 H, 2 H–C(2)); 3.65 (*s*, 3 H, CH_3O); 3.75 (*sext.*, $J = 7$, 1 H, H–C(7)); 5.55 (*m*, 2 H, CH=CH). – MS.: 172 (10, M^+), 155 (18), 154 (35), 139 (9), 128 (61), 113 (40), 95 (100), 94 (85), 81 (50), 74 (38), 67 (22), 55 (27), 45 (48), 43 (35), 29 (9), 18 (23).

Preparation of (+)-(S)-7-hydroxy-3-octenoic acid (**23**). A solution of (+)-*(S)*-**14ca** (1 g, 5 mmol) in water (10 ml) was cooled to 0°. Periodic acid (1.5 g, 6.5 mmol) in water (5 ml) was added slowly and the reaction mixture was stirred at RT. for 1 h. Workup as described for (±)-**23** furnished the (+)-(S)-acid **23** (0.776 g, 98%) as colorless oil, $n_D^{20} = 1.4772$, $[\alpha]_D^{20} = +28.8°$ ($c = 1$, $CHCl_3$). – ^{1}H-NMR. ($CDCl_3$) and IR. (film) were identical with the (±)-acid described above.

Preparation of (±)-cis-(6-methyl-2-tetrahydropyranyl)acetic acid (**22a**). To a solution of **15ca** (3.4 g, 17 mmol) in THF (10 ml) and water (5 ml) was added at 0° a solution of periodic acid (4.85 g, 22.5 mmol) in water (10 ml) and THF (5 ml). The reaction mixture was stirred at 0° for 12 h. The reaction mixture was poured into a mixture of sat. salt solution (50 ml) and ether (200 ml). It was extracted with ether. Workup as described for **23** furnished **22a** (2.68 g, 99%), m.p. 52° (hexane), mixed m.p. undepressed with authentic sample of (±)-**23a** prepared from (±)-**15ba**.

*Preparation of (+)-*cis*-(S,S)-(6-methyl-2-tetrahydropyranyl)acetic acid* (**22a**). A solution of periodic acid (3 g, 13 mmol) in water (8 ml) and THF (4 ml) was added to a solution of (+)-*(S,S)*-**15ca** (2 g, 10 mmol) in water (4 ml) and THF (8 ml) and stirred over night at 0°. Workup as in case of (+)-**22a** furnished the pure acid (+)-*(S,S)*-**22a** (1.9 g, 95%). Optical rotation, IR., and ^{1}H-NMR. were in agreement with the values observed for an authentic sample of (+)-*(S,S)*-**22a** prepared from (+)-*(S,S)*-**15ba**.

Preparation of (2-hexahydrochromanyl)acetic acid (**21b**). The hydroxyketone **15cc** (2.64 g, 11 mmol) furnished **21b** (2.15 g, 98%) following a similar procedure as for **22a**. M.p. 80–82° (from pentane/ether). – IR. (CCl_4): 3000, 2920, 2850, 1708, 1450, 1430, 1410, 1370, 1350, 1335, 1290, 1215, 1195, 1175, 1140, 1100, 1075, 990, 955. – ^{1}H-NMR. (CCl_4): 0.9–2.0 (*m*, 13 H, methylene H and H–C(4a′); 2.3 (*d* × *d*, $J = 15$ and 6, 1 H, H–C(2)); 2.57 (*d* × *d*, $J = 15$ and 6, 1 H, H–C(2)); 2.9 (m, 1 H, H–C(8a′)); 3.7 (*m*, 1 H, H–C(2′)), 10.7 (br. *s*, -OH). – MS.: 198 (5, M^+), 180 (14), 154 (16), 136 (18), 121 (19), 111 (12), 102 (13), 95 (14), 81 (80), 67 (100), 59 (60), 41 (55), 29 (23).

$C_{11}H_{18}O_3$ (198.2) Calc. C 66.64 H 9.15% Found C 66.61 H 9.10%

Preparation of trans*-5-(2-hydroxycyclohexyl)-(3*E*)-3-pentenoic acid* **24.** A solution of hydroxyketone **15cc** (2.33 g, 9.7 mmol) in THF (10 ml) and water (5 ml) was cooled to 0° and treated with a solution of periodic acid (2.88 g, 12.62 mmol) in water (10 ml) and THF (5 ml). The reaction mixture was stirred

over night at 0°. Workup as in case of **22a** furnished the acid **24** (1.88 g, 98.8%) as colorless oil. During attempted distillation under reduced pressure it turned slightly yellow. – IR. (film): 3300 br., 2930, 2860, 1710, 1460, 1450, 1405, 1290, 1195, 1120, 1060, 1030, 972, 925, 845, 820, 790, 755, 735. – ^{1}H-NMR. ($CDCl_3$): 1.23 (br. *m*, 6 H, all H_{ex}); 1.85 (br. *m*, 6 H, 4 H_{eq} and 2 H–C(5)); 3.03–3.4 (*m*, 3 H, 2 H–C(2) and H–C(1')); 5.63 (*m*, 2 H, CH=CH).

8. Ring-opening of THF- and THP-acetic acids with excess LDA. – *Preparation of 6-hydroxy-6,6-diphenyl-2-hexenoic acid* (**25a**) *and 6-hydroxy-6,6-diphenyl-3-hexenoic acid* (**25b**). To the cold (–78°) solution of LDA (3.5 mmol) in THF (8 ml) was added a solution of **16a**, (0.282 g, 1 mmol) in THF (2 ml) and HMPT (1 ml). After stirring over night (–78° to RT.) and adding acetic acid (at –78°), the reaction mixture was poured into water, acidified with 1N HCl and extracted with ether. The crude product after usual workup was purified by preparative layer chromatography (silicagel *PF254*, ethylacetate/pentane 35:65) furnished **25b**, (0.21 g, 74%).

If the acid **16a** (1 mmol) was reacted with LDA (2 mmol), it gave a mixture of **25a** and **25b** (**25a/25b** = 66:34). When reacted with 2.2 mmol of LDA, it gave **25a** (m.p. 137–138.5°) and **25b** in equal proportions, from which **25b** was separated by fractional crystallization (from ether).

Spectral data of **25a**. – IR. (KBr): 2500–3300, 1680, 1640, 1595, 1490, 1450, 1425, 1350, 1310, 1290, 1250, 1200, 1060, 960, 910, 880, 780, 750, 640, 600. – ^{1}H–NMR. ($CDCl_3$): 2.33 (*m*, 4 H, 2 H–(4 and 5)); 5.76 (*d*, *J* = 16, 1 H, H–C(3)); 7.0 (*m*, 1 H, H–C(2)); 7.33 (*m*, 10 H, aromat. H).

$C_{18}H_{18}O_3$ (282.3) Calc. C 76.57 H 6.43% Found C 76.46 H 6.56%

Spectral data of **25b**. – IR. (film): 2500–3500, 1710, 1655, 1600, 1495, 1450, 1180, 1100, 1060, 1010, 750, 700. – ^{1}H-NMR. ($CDCl_3$): 3.06 and 3.13 (2*d*, *J* = 6, 4 H, 2 H–C(2) and 2 H–C(5)); 5.6 (*m*, 2 H, CH=CH); 7.3 (*m*, 10 H, aromat. H).

Preparation of trans-*7-Hydroxy-2-octenoic acid* (**25c**). To the cold (–78°) solution of LDA prepared from diisopropylamine (2.75 ml, 19.5 mmol) and BuLi (12.5 ml of 1.6M solution in hexane) in THF (90 ml) was added a solution of the acid **22a** (1.58 g, 10 mmol) in THF (10 ml). The reaction mixture was stirred for 4 h (–78° to 0°) and then quenched with 1N HCl. It was poured into water and extracted with ether. Workup furnished a residue (1.55 g) which on fractional distillation gave **25c** (1.27 g, 80%), b.p. 200°/0.004 Torr. The acid thus obtained was pure enough for further reactions. – IR. (film): 3400, 2970, 2930, 2860, 1695, 1650, 1420, 1370, 1335, 1280, 1210, 1173, 1130, 1085, 1065, 1035, 995, 930, 870. – ^{1}H-NMR. ($CDCl_3$): 1.2 (*d*, *J* = 6, 3 H, H_3C–C(7)); 1.4–1.75 (*m*, 4 H, 2 H–C(5 and 6)); 2.25 (*m*, 2 H, 2 H–C(4)); 3.8 (*sext.*, *J* = 6, 1 H, H–C(7)); 5.5 (br. *s*, 2 H, 2 OH); 5.85 (*d* × *t*, *J* = 16 and 7, 1 H, H–C(2)); 7.05 (*d* × *t*, *J* = 16 and 7, 1 H, H–C(4)).

*Preparation of (+)-*trans-(S)-*7-hydroxy-2-octenoic acid* (**25c**). To a solution of diisopropylamine (3.40 ml, 24 mmol) in THF (80 ml) was added butyl lithium (15.5 ml of 1.6M solution in hexane, 24 mmol) at 0°. After stirring at 0° for 20 min, it was cooled to –78° and a solution of (+)-*(S,S)*-**22a** (1.896 g, 12 mmol) in THF (10 ml) was added with a syringe. The reaction mixture was stirred and allowed to warm up from –78° to 0° during 4 h. It was hydrolyzed with 1N HCl and extracted with ether. The aq. layer was saturated with salt and then extracted twice with ether. The combined organic phases were washed with sat. NaCl-solution and dried over $MgSO_4$. Removal of solvent under reduced pressure furnished (+)-*(S)*-**25c**. (1.51 g, 80%) as an oil, $[\alpha]_D^{22} = +12.64°$ ($c = 0.53$, $CHCl_3$). – ^{1}H-NMR. ($CDCl_3$): identical with (±)-acid-**25c**. – IR. ($CHCl_3$): 3600, 3400, 2970, 2930, 2860, 1695, 1650, 1450, 1410, 1375, 1282, 1220, 1120, 1090, 1040, 990, 980, 925, 910, 840.

This acid thus obtained was enough pure to carry out further reactions [19].

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