64. Synthesis of Optically Pure Compounds by Enantiotopically Differentiating Monoacetalization of Prochiral Diketones[1])

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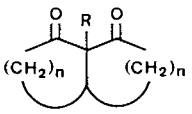
Summary

Reaction of 9-methyl-*cis*-decalin-1,8-dione (**2**) and of its *trans*-isomer (**3**) with (2*R*,3*R*)-2,3-butanediol (**8**) gives in both cases the monoacetals in high yield. While no enantiotopic differentiation is found for **3**, a strong preference for the (9*S*,10*R*)-monoacetal **9** is found for the *cis*-decalin-dione **2**. The differentiation, reaching a maximal ratio of 9:1, is found to increase by conditions, which slow down the rate of reaction, *e. g.* lowering the temperature, the concentration of the acid catalyst, or by using a sterically encumbered catalyst. The use of this procedure for the preparation of optically active compounds is exemplified by the transformation of monoacetal **9** (obtained in 76% yield from **2**) into (9*R*,10*R*)-9-methyl-1-decalone (**12**). The differing behaviour of diketones **2** and **3** is discussed in terms of steric and electronic effects.

1. Introduction. – The preparation of optically active compounds is one of the most important problems of synthetic organic chemistry. It is solved by either separating racemic mixtures, partial synthesis starting from available, mostly natural, optically active material, or by applying enantio-differentiating reactions.

In connection with our interest in the syntheses of terpenoid natural products, we envisaged the possibility of preparing optically active starting materials by enantiotopically differentiating reactions with prochiral *bicyclic* diketones of type **a**.



a

[1]) These results were presented at the „Herbstversammlung der Schweizerischen Chemischen Gesellschaft", October 16, 1981, in Bern.
The nomenclature and classification of stereodifferentiating reactions proposed by *Izumi & Tai* [1] are used in this communication.

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Differentiation of enantiotopic carbonyl groups turned out to be an excellent method, when applied to *monocyclic* prochiral 1,3-diketones. The pioneering work has been reported by *Weill-Raynal et al.*, who used the monohydrazone formation as differentiating process [2]. More recently *Hajos & Parish* obtained high optical yields in intramolecular aldol condensations catalyzed by proline [3]. Using chiral phosphines *Trost et al.* developed a promising variant of this approach in the form of a *Wittig*-type reaction [4].

As a first prochiral diketone, the 1,8-decalin-dione-system (**a**, n=3), and as differentiating reaction the monoacetalization with an optically active diol, were chosen by us. Enantiotopically differentiating *mono-derivatization* of prochiral substrates bearing two identical functional groups have the following advantages: *1*) the products are diastereomers and can therefore be separated; *2*) the pure diastereomers, when further transformed and deprotected, yield enantiomerically pure compounds; *3*) by changing the steps of such a reaction sequence, the product with the same absolute configuration can be obtained from either of the diastereomeric derivatives; *4*) if this is not practicable, the unwanted isomer can be converted back to the prochiral starting material, thus allowing a complete conversion to optically pure compounds independent of the degree of enantio-differentiation[3]). Except for the hydrazone formation of a 1,3-diketone mentioned above [2], this approach has been applied successfully mainly to the monoesterification of diols [5] [6] and enzymatic monohydrolysis of prochiral diesters [7].

2. Results. – Decalin-1,8-dione (**1**) was prepared according to published methods [8], and C-methylated by treating its sodium salt with methyl iodide in dimethoxyethane *(Scheme 1)*. Separation by column chromatography gave 54% 9-methyl-*cis*-decalin-1,8-dione (**2**) and 33% of its *trans*-isomer (**3**). The configurations of **2** and **3** were assigned by ^{13}C-NMR. and by comparing chemical reactivity *(vide infra)*. The ^{13}C-chemical shifts were inconclusive for this assignment, even when compared with the values of the parent 9-methyl-*cis*- and 9-methyl-*trans*-decalin [9]. However, when measured at –110°, four of the seven resonances, which form the ^{13}C-NMR. spectrum of **2** at room temperature, were found to split into two signals revealing dynamic effects of conformational mobility. The *cis*-decalin dione **2** is expected to exist as a rapidly interconverting racemic mixture of two chair/chair conformers (see the following stereochemical formulae of **2**). An energy of activation of 8.4 kcal/mol was determined for this racemization using the shift-difference (85 Hz) and the coalescence temperature (–95°) of the C(1)- and C(8)-carbonyl resonances[4]). As expected the ^{13}C-spectrum of the rigid 9-methyl-*trans*-decalin-1,8-dione (**3**) was insensitive to temperature changes.

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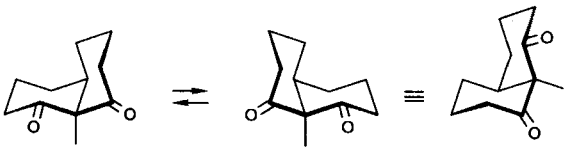
[3]) For a more extensive discussion see [5].

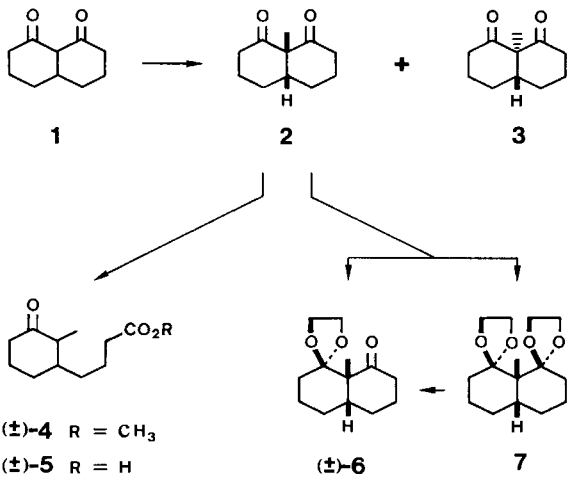
[4]) The same value resulted from a line shape analysis [10]. Compared with the value of *cis*-decalin, 12.0 kcal/mol, this low barrier is probably due to a reduction of torsional strain caused by the replacement of two methylene by two carbonyl groups. For a recent study of the complex chair/chair-conformer interconversions of *cis*-decalin see [11].



2 (M-Enantiomer) 2 (P-Enantiomer)

The structural assignment of **2** and **3** is further corroborated by their different chemical reactivity. On treatment with a 4% K_2CO_3-solution in methanol for 16 h at room temperature the *trans*-compound **3** remains unchanged, while the *cis*-isomer **2** undergoes smooth β-diketone cleavage *(Scheme 1)*, giving methyl ester **4** and the acid **5** (70% and 26% respectively); **5** can be transformed into **4**, by treatment with diazomethane. According to GC. and ^{1}H-NMR. analysis **4** is a (4:1)-mixture of 1′,2′-*trans*- and 1′,2′-*cis*-epimers[5]). The higher reactivity of **2** is explainable, since the hemiacetal intermediate can adapt its conformation in such a way, that the bond to be cleaved is axial in the cyclohexanone with the free carbonyl group, a geometrically ideal situation with nearly parallel σ- and π-orbitals allowing synchronous σ-bond cleavage and enol-π-bond formation (see *Scheme 4*, **A** and **C**). The rigid all-equatorial conformation in *trans*-decalin-dione **3** precludes such an array of reacting bonds.

Scheme 1



Before testing the reaction with chiral diols, the acetalization of 9-methyl-*cis*-decalin-1,8-dione (**2**) with ethyleneglycol was studied. Normal conditions using a *Dean-Stark* trap, *p*-TsOH as catalyst, and 1.15 mol-equiv. of glycol resulted in a 78% conversion of **2**, yielding 64% (82% based on consumed **2**) of monoacetal **6** and

[5]) Under these non enantio-differentiating reaction conditions racemic products result from the β-diketone cleavage. It is however planned to test this smooth transformation for asymmetric induction by either using a chiral catalyst or a chiral nucleophile.

4% (5% based on consumed **2**) diacetal **7**, with 5 mol-equiv. of diol, however, 45% monoacetal **6** and 39% diacetal **7** were isolated. The diacetal **7** could be converted into **6** in 80% yield by treatment with acetone/*p*-TsOH, thus ensuring an ultimately high-yield overall conversion of dione **2** into the mono-derivative **6**[6]).

For the enantiotopically differentiating monoacetalization of the prochiral diketones **2** and **3** (–)-(2*R*,3*R*)-2,3-butanediol (**8**) was chosen[7]). It is readily available in both enantiomeric configurations and in high optical purity [14]. Its symmetry precludes the formation of epimeric acetals. It has been successfully applied as a chiral derivatization agent for the separation of racemic carbonyl compounds (*e. g.* [14b, c]).

On reaction of 9-methyl-*cis*-decalin-1,8-dione (**2**) with 1.1 mol-equiv. of diol **8** using 5 mol % *p*-TsOH as catalyst and continuously removing the water by azeotropic distillation with benzene, GC.-analysis of the reaction mixture showed two products and some starting material. This mixture could be separated by column chromatography into 24% starting material **2**, 50% of a crystalline monoacetal **9**, and 15% of a diastereomeric monoacetal **10**. Among the by-products formed in minor quantities some diacetal **11** *(vide infra)* could be identified *(Scheme 2)*. The structures, except for the absolute configurations of **9** and **10**, were assigned by spectroscopic analysis[8]). Dione **2** can thus be monoacetalizated with the chiral diol **8** in high yield (85% based on consumed **2**) and with promising enantio-differentiation (77:33, determined by GC.).

The specific rotations and the CD.-spectra of monoacetals **9** and **10** are dominated as expected by the influence of the keto function and therefore opposite in sign. The CD.-spectrum of the major isomer **9** exhibits a positive maximum at 304 nm with a $\Delta\varepsilon$ of +0.916. For **10** a value of –0.749 was found. Unfortunately no unambiguous conclusions can be drawn from these data, since no increments are available for O-containing groups situated in the front octants. The absolute configurations of **9** and **10** were therefore derived by chemical transformation to (+)- and (–)-9-methyl-*cis*-1-decalone ((+)- and (–)-**12**). This was effected by first treating **9** and **10**, respectively, with *p*-tolylsulfonylhydrazide, reducing the hydrazones **13** and **14** with catecholborane [15], and finally treating the resulting acetals **15** and **16** with dilute acid in ethanol. Starting from **9** the resulting decalone **12** had a specific rotation of +30.5°; on the other hand –30.7° was the value of **12** derived from **10**. Since +32.7° has been reported for (9*R*,10*R*)-9-methyl-*cis*-1-decalone ((+)-**12**) [16], the monoacetal **9** has (9*S*,10*R*)- and its isomer **10** (9*R*,10*S*)-configuration. The overall yields of the conversions **9** → (+)-**12** and **10** → (–)-**12** were 52% and 51% respectively.

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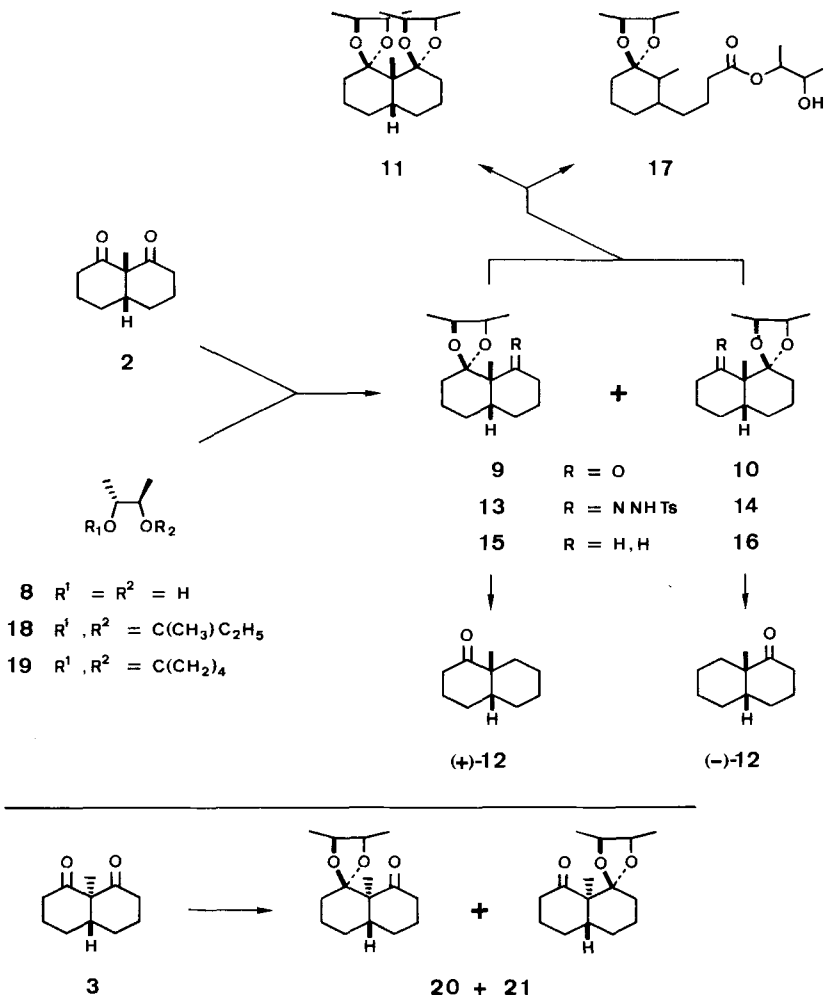
6) This high yield mono-derivatization of a substrate with two identical functions is due to different rates of the first and the second acetalization step [12]. Selective mono-acetalization was recently applied with success in a synthesis of (±)-isocomene [13].

7) Another suitable diol, dimethyl tartrate, failed to react with dione **2**.

8) The ^{1}H- and ^{13}C-NMR. spectrum of the sterically congested diacetal **11** at room temperature showed significantly broadened signals due to dynamic effects. The ^{1}H-NMR. spectrum of **11** remained broadened to some extent even at 75°. At –20° the ^{13}C-NMR. spectrum at 75.5 MHz consisted of 37 resolved signals, which can be attributed to the 38 C-atoms of the two diastereomeric chair/chair-conformers of **11**. A rough estimation resulted in an inversion barrier of 15–16 kcal/mol. The NMR. spectra of the bis(spiroacetal) **7** *(Scheme 1)* exhibited similar effects.

Scheme 2



Further work was done on optimizing this process, *i. e.* specifically improving the yield of **9**. Additional experiments using azeotropic distillation for the removal of water are shown in the first 5 lines of *Table 1*: an excess of diol **8**, different reaction temperature in other solvents, or a different catalyst give some minor changes in product distribution, which are however difficult to rationalize. Among the other acetalization methods [17][9]) the use of water absorbing molecular sieves [18] seemed

[9]) Anhydrous $CuSO_4$ as water absorbent prooved to be inadequate, since it absorbed the diol **8** and removed it from the reaction system faster than the rate of acetalization. With $BF_3 \cdot Et_2O$ as reagent [19] the dione **2** was decomposed. Treatment of dione **2** with the bis(trimethylsilyl)ether of diol **8** and a catalytic amount of trimethylsilyl trifluoromethansulfonate at low temperature, according to a novel spiroacetalization method [20], gave a low degree of differentiation (54/46) and incomplete reaction (46% conversion).

very promising and finally emerged as the method of choice *(Table 1*, lines 6–10) for the acetalization of **2**, with preparatively best results obtained by using a slight excess of diol **8**, a sterically crowded acid catalyst, room temperature, and benzene as solvent *(Exper. 7)*. The major monoacetal **9** is thereby isolated in a 76% yield, the enantiotopic differentiation being 7.3:1. Higher temperature led to decreased yield and selectivity *(Exper. 6)*, while reaction at 5° led to a high degree of differentiation (9:1), but slow reaction rates *(Exper. 8)*. A large excess of diol **8** has no pronounced effect *(Exper. 9)*. Cyclohexane was found less suitable as solvent than benzene *(Exper. 10)*, while no acetalization was observed in THF and *t*-butyl alcohol.

Table 1. *Conditions and results of experiments 1–10*

Exper.[a])	Method[b])	Solvent	(Temp.)	Mol-equiv. diol **8**	Catalyst[c])	Time (h)	Conversion (%)	Yield (%) of **9**+**10**[d])	Ratio **9**/**10**[e])	Yield (%) of **11**
1	A	C_6H_6	(80)	1.1	*p*-TsOH	18	76	65 (85)	77:23	<1
2	A	C_6H_6	(80)	5.0	*p*-TsOH	6	100	84 (84)	80:20	9
3	A	$CH_3C_6H_5$	(110)	1.1	*p*-TsOH	18	61	53 (87)	85:15	<1
4	A	CH_2Cl_2	(40)	1.1	*p*-TsOH	22	83	72 (87)	75:25	2
5	A	C_6H_6	(80)	1.2	RSO_3H[f])	5	85	71 (83)	82:18	2
6	B	C_6H_6	(80)	1.2	RSO_3H[f])	48	66	59 (89)	82:18	<1
7	B	C_6H_6	(RT.)	1.2	RSO_3H[f])	72	97	87 (90)	88:12	5
8	B	C_6H_6	(5)	1.2	RSO_3H[f])	120	92	83 (89)	90:10	5
9	B	C_6H_6	(RT.)	5.0	RSO_3H[f])	60	96	83 (86)	86:14	7
10	B	C_6H_{12}	(RT.)	1.2	RSO_3H[f])	120	67	60 (89)	84:16	3

a) Corresponds to numbering in the *Experimental Part*.
b) A: removal of water by azeotropic distillation; B: removal of water with molecular sieves 5A (*ca.* 0.5 g/mmol **2**).
c) Method A: 3–5 mol %; Method B: 9–11 mol %.
d) Absolute yield of isolated products, in parentheses yield based on consumed **2**.
e) Determined by GC.
f) R = Mesityl.

In *Table 2* the effects of the acid catalyst are summarized: the selectivity decreases with increasing catalyst concentration *(Exper. 11, 7* and *12, 14* and 15), high differentiation (9:1), unfortunately accompanied by a slow and incomplete conversion, is observed on lowering the amount of catalyst *(Exper. 12)*. The degree of differentiation is also strongly influenced by the nature of the catalyst, with bulky sulfonic acids giving the best results *(Exper. 7* and *16)*. A ratio of **4**:1 was found for the other sulfonic acids studied *(Exper. 17–19)*; the p*K* of the acid seems to have no significant influence. Possible adsorption of the acid catalyst by the molecular sieves [18], studied by pre-treating the sieves with the catalyst *(Exper. 13)*, was found to play no part. No acetalization was observed with acid treated molecular sieves [18], pyridinium *p*-toluenesulfonate, or pyridinium trifluoroacetate as catalyst; and trifluoromethanesulfonic acid and strongly acidic ion-exchange resins were also

found unsuitable *(Exper. 20* and *21)*[10]). But for the use of these two catalysts the yields of monoacetals **9** and **10** based on consumed diketone **2** were high (83–91%, *Tables 1* and *2*). However the interpretation of minor changes of the ratio **9/10** requires precaution, since it not only reflects the degree of enantiotopic differentiation, but is also influenced by secondary reactions, which do not necessarily proceed at the same rate for **9** and **10**. Examples of such processes are the ring cleavage leading to **17**[10]) and the formation of diacetal. The latter, a slow process, was indeed found to be faster for the minor monoacetal **10** with a yield of 62% (91% based on consumed **10**) after 7 days of reaction. After 12 days only 22% of **11** (61% based on consumed starting material) were isolated from acetalization of **9**. The diastereomer differentiation observed for the second acetalization thus shows the same order of preference as the enantiotopic differentiation of the monoacetalization.

Table 2. *Conditions and results of experiments 11–21*[a])

Exper.[b])	Catalyst	(mol %)	Time (h)	Conversion (%)	Yield (%) of **9** & **10**[c])	Ratio **9/10**[d])	Yield (%) of **11**
11	Mesitylenesulfonic acid	(20)	19	100	84 (84)	83:17	6
7	Mesitylenesulfonic acid	(9)	72	97	87 (96)	88:12	5
12	Mesitylenesulfonic acid	(4)	288	52	44 (85)	90:10	< 1
13	Mesitylenesulfonic acid[e])	(9)	72	94	86 (91)	89:11	3
14	Naphtalenesulfonic acid	(18)	8	98	77 (89)	76:24	7
15	Naphtalenesulfonic acid	(10)	27	93	85 (91)	81:19	1
16	2,4,6-Tri-2'-propylbenzenesulfonic acid	(10)	72	93	82 (88)	90:10	5
17	*p*-Toluenesulfonic acid	(11)	22	98	88 (90)	81:19	5
18	*p*-Methoxybenzenesulfonic acid	(10)	24	100	88 (88)	81:19	5
19	Methanesulfonic acid	(12)	22	98	85 (87)	80:20	5
20	Trifluoromethanesulfonic acid	(10)	6	84	55 (65)	63:37	8[f])
21	*Amberlyst 15 (H^+)*		120	76	36 (47)	76:24	2[g])

a) Method B (see *Table 1*), in benzene at RT. with 1.2 mol-equiv. of diol **8**.
b) Corresponds to numbering in the *Exper. Part.*
c) Absolute yield of isolated products, in parentheses yield based on consumed **2**.
d) Determined by GC.
e) Before adding the reactants, the molecular sieves were stirred for two days with the acid catalyst in benzene.
f) In addition 18% of the monocyclic ester **17** were isolated.
g) In addition 33% of **17** were isolated.

Acetalization of 9-methyl-*cis*-decalin-1,8-dione (**2**) with butanediol **8** gives the monoacetals **9** and **10** in high yield, the enantiotopic differentiation resulting from *kinetic* control of reaction reaching values as high as 9:1. In order to evaluate the ratio under thermodynamic control of reaction, the equilibration of the diastereomeric monoacetals **9** and **10** was studied. Acid treatment of **9** or **10** in benzene, CCl_4, or acetone with or without added diketone **2** however gave only decomposition with no

10) Considerable amounts of a further product, the monocyclic ester **17** *(Scheme 2)* were formed. This and some similar transformations are under investigation [21].

observable isomerization[11]). Another possibility for studying relative thermodynamic stabilities of acetals is the transacetalization of ketone/acetal mixtures catalyzed by acids and a small amount of diol [17] [23]. When dione **2** was treated with two mol-equiv. of either acetal **18** or **19**, which were prepared by acetalization of 2-butanone and cyclopentanone respectively, monoacetalization occured to the extent of 30–35% *(Scheme 2)*. The low yield with only 40% starting material recovered again prevents a conclusive interpretation. By monitoring the course of the reaction (GC.), it was found, that the initial ratio of the products (5:1 at 15% conversion) dropped slowly to a constant value of 2.2:1. This change proceeded after the completion of the transacetalization of acetals **18** or **19** and diketone **2**; it could therefore be the result of either an equilibration of the monoacetals **9** and **10**, or a diastereomer-differentiating ring cleavage to ester **17**[10]) preferring **9**. From the reaction with **18** 17% of **17** were indeed isolated.

When 9-methyl-*trans*-decalin-1,8-dione (**3**) was acetalized with diol **8**, monoacetals **20** and **21** were formed in high yield *(Scheme 2)*. No diacetal was formed using either method A or B, contrary to the findings in the *cis*-series. Monoacetals **20** and **21** were inseparable by column chromatography or capillary-GC. According to ^{1}H-NMR. analysis (300 MHz) enantiotopic differentiation was very low, 52:48 under both conditions.

3. Discussion. – The high-yield monoacetalization of 9-methyl-*cis*-decalin-1,8-dione (**2**) and of its *trans*-isomer (**3**) shows, that these processes are well suited for enantiotopic differentiation. The degree of differentiation is however very different for these two closely related substrates. In order to convert all prochiral starting material to optically active compounds, a high degree of selectivity is not necessary, provided the diastereomeric derivatives can be separated, but low or no differentiation is impracticable (see *Introduction* and [5]). The reason for the different behaviour of **2** and **3** is therefore of interest. As has been shown, the preferred formation of monoacetal **9** from **2** is due to a kinetic factor and is not the result of a thermodynamically controlled reaction[12]). Thus, it is the reaction mechanism, which is responsible for enantiotopic differentiation. The course of a spiro-acetalization is shown in *Scheme 3*: acid- or base-catalyzed hemiacetalization *(step 1)* is followed by protonation *(step 2)*; the following rate determining step is generally written as a S_N1-type process *(step 3* and *4)*. In the case of spiro-acetalization *step 4* is an unfavor-

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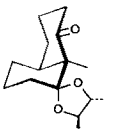
[11]) Isomerizations of monoacetals were observed in the case of asymmetrically substituted indane-1,3-diones [22].

[12]) According to molecular models isomer **9** is expected to be only slightly more stable than **10**. If the "outside"-conformation is assumed to predominate for both isomers (see the following stereochemical formulae for **9** and **10**), the only difference between **9** and **10** is found among the distances of the 9-methyl- and the acetal methyl-groups. This is reflected in the ^{13}C-NMR. spectra of **9** and **10**, where main differences are restricted to the 9-methyl- and the spiroacetal C-atoms. The resonances of the ring-C-atoms are almost identical for **9** and **10**.



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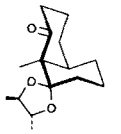

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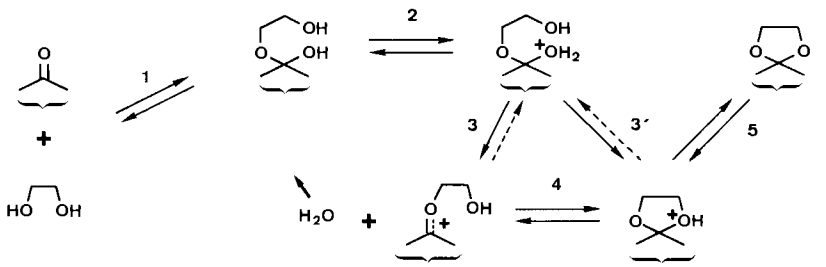
able "5-endo-trig" cyclization, a S_N2-path *(step 3')* has therefore been proposed as an alternative [24]. Calculations have however shown, that the torsion-energy is considerably lower for an oxacarbenium ion than for an olefinic double-bond, and that constraints imposed by *Baldwins* rules [25] are thus less severe for spiro-acetalization [26][13]). Deprotonation *(step 5)* finally gives the product. The acetalization is a reversible process, but by efficient removal of water from the reaction mixture the rate determining *step 3*[14]) becomes irreversible and the following *steps 4* and *5* have no influence on enantiotopic differentiation. The monoacetalization of prochiral diketones with chiral diols is thus controlled by the relative stabilities of the equilibrated diastereomeric hemiacetals, and by differences in the rate-determining oxacarbenium-ion formation *(step 3)*.

Scheme 3



Before turning to the more complex situation with the chiral diol **8**, the acetalization of diketones **2** and **3** is discussed for a general symmetric case. In *Scheme 4* all possible hemiacetals of **2** (**A–D**) and **3** (**E** and **F**) are depicted; **A** and **B**, **C** and **D** are interconverted by ring inversion[15]). A very important point controlling the reactive conformation of the alcohol side-chain is the anomeric effect [29], which is expected to dominate the rates of *step 3 (Scheme 3)*. Each of the hemiacetals **A–F** can adapt two conformations with one of the OR-lone-pairs antiperiplanar to the C,OH-bond; in *Scheme 4* the ones with the R-group in the less hindered positions are shown (see however **B'** and **E'**, *Scheme 6*). It is evident, that hemiacetal-structures **A** and **C** have no influence on the acetalization of **2**. With their unfavorable *"inside"*-conformation they represent only minor components of the equilibrated mixture. They have furthermore the ideal array of bonds for the β-diketone cleavage, a process, which is

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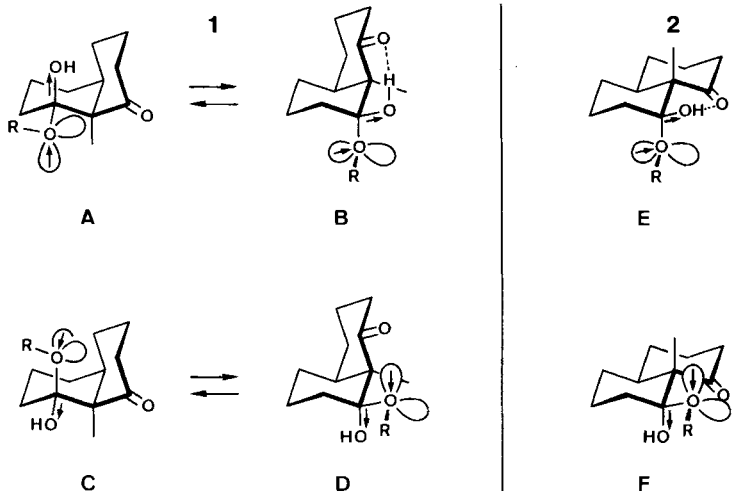
13) In the following discussion only the conventional mechanism is therefore considered.

14) In a recent report *step 4* is considered to be rate determining [27]. This would mean, that the barrier of this cyclization is high in energy [26], since it is the rate-determining step of the reverse process, the acetal hydrolysis [28].

15) Each of the structures **A–F** is a racemic mixture, if the alcohol residue (R) is achiral. In *Scheme 4* only the (9*S*,10*R*)-series is shown for **2**, the (9*R*,10*R*)-series for **3**. The double number of different hemiacetals for the *cis*-decalin dione **2** reflects, that this compound is actually not prochiral, but a fast equilibrating racemic mixture. Asymmetric inductions observed in reactions of **2** are therefore correctly defined as *"enantiomer-differentiating"* [1]. However, if much faster rates are assumed for the ring-inversion than for the differentiating process, this has no influence on the product distribution.

observed in the base-catalyzed hemiacetalization of **2** with methanol *(Scheme 1)*. The resulting bond-polarization with positive charge on the hemiacetal-C-atom disfavors the loss of water from these conformers.

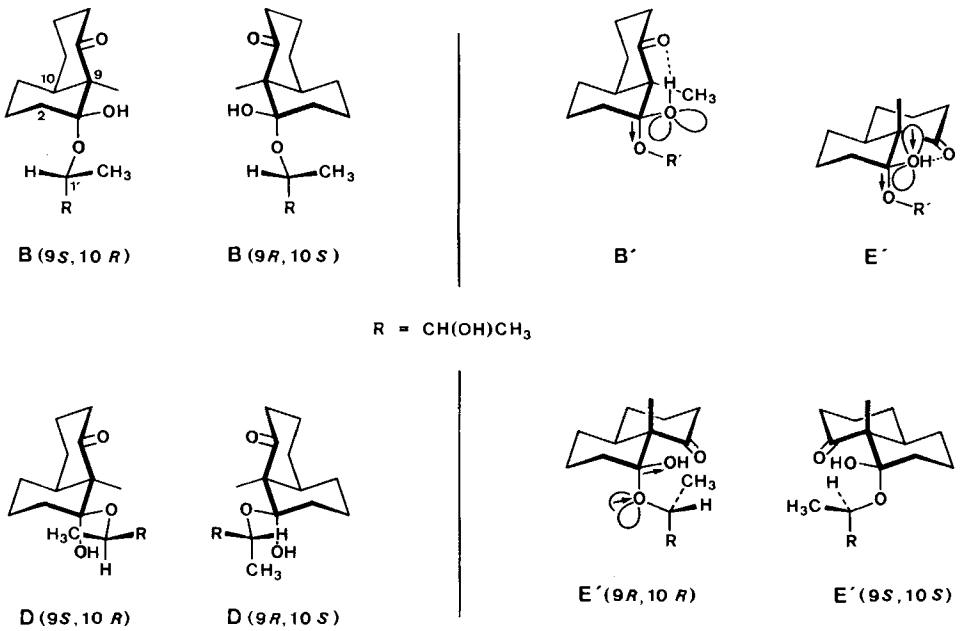
Scheme 4



It is difficult to arrive at a decision concerning **B** or **D** for **2**, and **E** or **F** for **3**: possible factors affecting thermodynamic stabilities are the H-bonds in **B** and **E** *vs.* destabilizing lone-pair interactions in **D** and **F**. As for possible kinetic factors, the loss of water might be somewhat better from the axial positions in **D** and **F** [30]. It is important to note, that the environment of OR is identical for **B** and **E** and for **D** and **F**. The following discussion concerning the influence of a chiral OR-group can therefore be restricted to the hemiacetals **B** and **D**. The same conclusions are valid for **E** and **F** derived from **3**.

Scheme 5 shows the 4 diastereomeric hemiacetals derived from (2*R*,3*R*)-2,3-butanediol (**8**) with the optimal conformations of the side-chains. The more remote center of chirality (R), which has only a marginal influence on enantiotopic differentiation, is the largest substituent of C(1'), and occupies therefore the sterically least congested site. For both structures **B** and **D** the crucial interactions are found to be the *"skew-pentane"*-relations between the methyl group of diol **8** and either C(2) of the decalin ring or the OH-group. With the first interaction being more severe this means that the (9*S*,10*R*)-isomer is preferable for **B** and the (9*R*,10*S*)-isomer for **D**. In the case of *trans*-isomer **3** the same arguments lead to (9*R*,10*R*)-preference for **E** and (9*S*,10*S*)-preference for **F**.

Scheme 5 *Scheme 6*



It follows from the experimental results that in the case of dione **2** with preferred formation of the (9*S*,10*R*)-monoacetal **9** the hemiacetal **B** is the favored intermediate. The low selectivity observed for **3** could be explained by involving both hemiacetals **E** and **F** (see however **E′**, *Scheme 6*). It is obvious, that more subtle differences have to be considered, in order to explain these results. Among the rate constants determining the thermodynamic equilibrium of hemiacetals **B**/**D** and **E**/**F**, respectively, the ones controlling the formation of **B** and **E** correspond to the preferred nucleophilic additions to diketones **2** and **3**[16]). Especially unfavorable, on the other hand, is the formation of **D**; this hindered attack to the concave side of *cis*-decalin-dione **2** could be too slow, to allow an equilibration of **B** and **D**, thus giving a possible explanation for the preferred reaction from intermediate **B**. In the case of the *trans*-isomer **3**, the formation of **F** is less biased. Another important point is the influence of the acid catalyst on the rate and enantiotopic differentiation of the acetalization. The general mechanism depicted in *Scheme 3* corresponds to specific acid catalysis. At high acid concentrations, however, general acid catalysis, *i.e.* simultaneous protonation *(step 2)* and loss of water *(step 3)*, has been observed [27]. In the case of dione **2**, it was found, that the rates and degree of enantiotopic differentiation are influenced by the steric bulk of the acid. This effect must also have its counterpart in the accessability of the hemiacetal OH-group, with the axial OH-

16) Monoreduction of diketone **2** with Li[HAl(*t*-BuO)$_3$] gives epimeric alcohols with configurations corresponding to those of hemiacetals **B** and **D** (replacement of OR by H) in a ratio of 37:1. A (15:1)-epimer ratio is the result of the reduction of isomer **3** [31].

group in **F** derived from **3** being less hindered than the OH-group in **D** derived from **2**. The epimeric hemiacetals, **B** derived from **2** and **E** derived from **3**, can adapt a conformation with a H-bond to the free carbonyl-group *(Scheme 4)*. As shown in *Scheme 6* for the conformers **B'** and **E'**, the H-bond in **B**, but not in **E**, inhibits optimal geometry with one of the OH-lone-pairs anti-periplanar to the C,OR-bond. The energy of this anomeric effect, 3–5 kcal/mol [29a], might be high enough to prevent H-bond formation in hemiacetal **B**[17]). One possible consequence of this might be easier protonation of **B**, if compared with the corresponding H-bonded **E**.

Still another explanation for the low degree of differentiation for diketone **3** is possible, if an alternative conformation of the hemiacetal side-chain is considered (**B'** & **E'**, *Scheme 6*). The different steric requirements of a carbonyl- *vs.* a methyl group make the conformer **E'** less biased than **B'**. As depicted in *Scheme 6*, the (9*S*,10*S*)-configuration would result from **E'**, which is the opposite preference of conformer **E** *(vide supra)*.

No definite rationalization explaining both, the high enantiotopic differentiation found for the monoacetalization of 9-methyl-*cis*-decalin-1,8-dione (**2**) and the low selectivity in the case of the *trans*-isomer **3**, can be given at present. Reasonable explanations result, if kinetic control of hemiacetalization, general acid catalysis of the acetalization, or different relative energies for corresponding hemiacetal-conformers of **2** and **3** are assumed.

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Experimental Part

General Remarks. The usual *workup procedure* consists in dissolving the reaction mixture in an organic solvent and water, extracting the aqueous phase 3 times with this solvent, washing the organic phases separately with satd. NaCl-solution to neutrality, drying with $MgSO_4 \cdot 2\ H_2O$, and evaporating the solvent on a rotary-evaporator. *Products.* (–)-(2*R*,3*R*)-2,3-butanediol (**8**) was purchased from *Fluka AG*, CH-9470 Buchs. *Chromatographic Separations* have been done with silicagel 60 (0.063–0.200) (*Merck*, or *Machery-Nagel & Co.*) using simple multi-bore columns [32]. For small scale separations and for "flash-chromatography" [33] silicagel 60 (0.040–0.063) *(Merck)* was used in normal columns. The collected fractions are listed in the order of elution. For *thin layer chromatography* (TLC.) precoated TLC.-plates *"silicagel 60 F 254" (Merck)* were used. The spots were observed using UV.-light (254 nm), or by coloration with either iodine vapors, or by spraying with a solution of 1% $Ce(SO_4)_2 \cdot 4\ H_2O$ and 2% $H_3[P(MoO_{10})_4] \cdot aq$ in 10% sulfuric acid [34] and heating. *Gas-liquid-chromatographic* (GC.) analyses of product ratios have been done using a *Carlo-Erba HRGC*-instrument connected to an automatic digital integrator. A capillary column (20 m, 0.33 mm diameter, *Pyrex*) coated with *UCON 50HB5100* was used. Retention times (t_R) are given in min. The *melting points*, which are non-corrected, have been measured in open capillaries immersed in a thermostated oil-bath (*Büchi 510*-apparatus). The *specific rotations* ($[\alpha]_D$) are been determined on a *Perkin-Elmer Spectrometer 241* using a 1 dm cell. The UV. spectra have been determined on a *Perkin Elmer Spectrophotometer 555* (λ_{max} in nm, ε-values in parentheses). The *CD.-spectra* have been recorded on a *Jobin-Yvon Mark III* instrument. The *IR. spectra* have been recorded on a *Perkin-Elmer Spectrophotometer 297*. The positions of absorption maxima are listed in cm^{-1}, the symbols *s, m,* and *w* stand for strong, medium, and weak. The *^{1}H-NMR. spectra* have been measured at frequencies of 80 MHz *(Bruker WP-80)*, 90 MHz *(Varian EM-390)*, 100 MHz *(Varian HA-100)*, and 300 MHz *(Bruker WM-300)*. The chemical shifts are listed in ppm (δ-values), the coupling constants in Hz.

[17]) In the absence of an anomeric effect, *i.e.* for the alcohols corresponding to **B** and **E**, strong H-bonds have been observed in non-polar solvents [31].

The multiplicity of the signals is indicated by the symbols *s*=singulet, *d*=doublet, *t*=triplet, *qa*=quadruplet, and *m*=multiplet, broad non-splitted signals are characterised by *m*, $w^{1/2}$ giving the width at half height. The *^{13}C-NMR.-spectra* have been measured at either 25.2 MHz *(Varian XL-100)* or 75.4 MHz *(Bruker WM-300)*. The chemical shifts, measured by broad band proton-decoupling, are given in ppm (δ-values). The multiplicity of the signals, evident from the structural assignments, have been determined either by single frequency off-resonance proton-decoupling, or by gated spin-echo techiques [35]. The *mass spectra* have been recorded on a *Hitachi-Perkin-Elmer RMU-6M* spectrometer. Relative peak intensities are given in percent of the base-peak (100%). If nothing is mentioned, the samples have been introduced indirectly and were ionized at 70 eV/200°. Direct injection = DI.

Abbreviations: RT. = room temperature, HV. = high vacuum, MAS = Mesitylenesulfonic acid·2 H_2O.

Methylation of decalin-1,8-dione (**1**). To a solution of 2.185 g (13.16 mmol) dione **1** [8] in 100 ml of benzene/ethanol 2:1 6.5 ml (13 mmol) 2N NaOH were added. After stirring for 5 min the solvents were evaporated under reduced pressure, and the residue was dried at HV. A suspension of the crystalline sodium salt in 100 ml of dimethoxyethane and 2.2 ml (5.01 g, 35.3 mmol) CH_3I was stirred at RT. for 8.5 h (Ar), quenched with 50 ml 1N HCl, and worked up in the usual way by extraction with ether. Prior to evaporation, the organic phase was decolorized by treatment with 0.5 g *Norite*. The products were separated by chromatography on 100 g silicagel. Elution with hexane/ether 2:1 gave 0.10 g (5%) **1** (starting material), 1.28g (54%) *cis*-dione **2**, and 0.78 g (33%) *trans*-dione **3**.

*Data of 9-methyl-*cis*-decalin-1,8-dione* (**2**). M.p. 30–31° (pentane). – IR. (CCl_4): 2990*m*, 2940*s*, 2870*m*, 1720*s*, 1703*s*, 1465*m*, 1460*m*, 1445*m*, 1425*m*, 1377*m*, 1340*w*, 1317*m*, 1312*m*, 1298*w*, 1262*m*, 1235*m*, 1200*w*, 1160*w*, 1145*m*, 1140*m*, 1097*s*, 1072*m*, 1055*m*, 1037*w*, 988*m*, 980*w*, 940*m*, 907*m*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 1.41 (*s*, H_3C–C(9)); 1.4–2.3 (*m*, 9H); 2.2–2.7 (*m*, 2 H–C(2,7)). – The ^{13}C-NMR. spectrum has been recorded at 25°, –40°, –60°, –66°, –71°, –75°, –80°, –86°, –89°, –94°, –99°, –105°, –107°, and –110°. – ^{13}C-NMR. (25.2 MHz, CD_2Cl_2, 25°): 19.7 (H_3C–C(9)); 24.1 (C(3,6); 27.4 (C(4,5)); 39.5 (C(2,7)); 48.0 (C(10)); 64.5 (C(9)); 211.4 (C(1,8)). – ^{13}C-NMR. (25.2 MHz, CD_2Cl_2, –110°): 19.7 (H_3C–C(9)); 22.3 and 25.7 (C(3,6)); 25.7 and 28.3 (C(4,5)); 38.1 and 40.9 (C(2,7)); 47.1 (C(10)); 64.2 (C(9)); 211.8 and 215.2 (C(1,8)). – MS.: 180 (45, M^+), 165 (2), 162 (3), 152 (23), 137 (23), *124* (100), 111 (36), 109 (23), 96 (27), 81 (23), 67 (18), 55 (36), 41 (27), 27 (14).

$C_{11}H_{16}O_2$ (180.24) Calc. C 73.30 H 8.95% Found C 73.15 H 8.84%

*Data of 9-methyl-*trans*-decalin-1,8-dione* (**3**). M.p. 55–56° (pentane/ether). – IR. (CCl_4): 2950*s*, 2870*m*, 1735*s*, 1697*m*, 1465*m*, 1450*m*, 1430*m*, 1370*m*, 1330*w*, 1310*m*, 1260*s*, 1220*w*, 1105*m*, 1060*m*, 1030*w*, 985*w*, 940*m*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 1.37 (*s*, H_3C–C(9)); 1.5–2.1 (*m*, 9H); 2.0–2.7 (*m*, 2 H–C(2,7)). – ^{13}C-NMR. (25.2 MHz, CD_2Cl_2, 25°): 16.0 (H_3C–C(9)); 23.4 (C(3,6)); 25.3 (C(4,5)); 37.8 (C(2,7)); 44.3 (C(10)); 61.9 (C(9)); 209.7 (C(1,8)). – ^{13}C-NMR. (25.2 MHz, CD_2Cl_2, –110°): 16.6 (H_3C–C(9)). 23.5 (C(3,6)); 25.1 (C(4,5)); 38.2 (C(2,7)); 43.8 (C(10)); 61.4 (C(9)); 212.1 (C(1,8)). – MS.: 180 (43, M^+), 165 (2) 162 (3), 152 (10), 137 (17), *124* (100), 111 (23), 108 (27), 96 (33), 81 (23), 67 (20), 55 (33), 41 (27), 27 (17).

$C_{11}H_{16}O_2$ (180.24) Calc. C 73.30 H 8.95% Found C 73.16 H 8.89%

Treatment of diketone **2** *with K_2CO_3 methanol.* A solution of 195 mg (1.083 mmol) diketone **2** in 5 ml methanol saturated with anhydrous K_2CO_3 (*ca.* 4%) was stirred for 16 h at RT. in an Ar-atmosphere. The mixture was diluted with ether and extracted 3 times with aqueous K_2CO_3-solution. Usual workup and "Kugelrohr"-distillation (120°/0.01 Torr) gave 160 mg (70%) of **4**, a 81:19 mixture of *trans*- and *cis*-isomer, determined by GC.-analysis (160°, 0.35 kg/cm^2, *trans*: t_R 5.6 min, *cis*: t_R 6.0 min). Acidification of the aqueous phase with 1N HCl and normal workup gave 57 mg (26%) of acid **5** (see below), which could be converted to **4** by treatment with ethereal diazomethane.

*Data of methyl 4-(*t*-2-methyl- and 4-(*c*-2-methyl-3-oxo-*r*-1-cyclohexyl)butanoate* (**4**). – IR. (CCl_4): 2940*s*, 2870*m*, 1740*s*, 1710*s*, 1447*m*, 1435*m*, 1380*w*, 1360*m*, 1345*w*, 1340*w*, 1312*m*, 1250*m*, 1195*s*, 1172*s*, 1155*m*, 1090*w*, 1055*w*, 988*w*, 960*m*, 882*w*. – ^{1}H-NMR. (300 MHz, $CDCl_3$): 1.01 and 1.05 (2*d*, J=7 and 6.5, H_3C–C(2')); 1.2–2.7 (*m*, 14 H); 3.67 and 3.68 (2*s*, H_3CO–C(1)). – MS.: 212 (5, M^+), 197 (2), 194 (3), 181 (2), 163 (2), 151 (4), 141 (3), 135 (9), 123 (4), *111* (100), 95 (5), 81 (10), 74 (12), 67 (7), 55 (20), 43 (9), 41 (13).

*Data of 4-(*t*-2-methyl- and 4-(*c*-2-methyl-3-oxo-*r*-1-cyclohexyl)butanoic acid* (**5**). – IR. ($CHCl_3$): 3670*w*, 3510*m*, 3600–2300*s* br., 1700*s*, 1445*m*, 1410*m*, 1378*w*, 1340*w*, 1310*w*, 1275*m*, 1130*w*, 1085*w*, 1055*w*, 960*m*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 1.00 and 1.04 (2*d*, J=7 and 7, H_3C–C(2')); 1.0–2.8 (*m*, 14

H); 8.5–9.0 (*m*, HO–C(1)). – MS.: 198 (14, M^+), 183 (2), 180 (4), 154 (7), 151 (10), 137 (4), 127 (7), 124 (6), 120 (2), *111* (100), 97 (11), 95 (7), 93 (4), 83 (16), 82 (18), 81 (12), 79 (12), 69 (12), 67 (11), 55 (35), 41 (23), 27 (5).

Acetalization of dione **2** *with 1,2-ethanediol.* – a) *With 1.15 mol-equiv. diol.* A solution of 180 mg (1.00 mmol) dione **2**, 64 µl (71 mg, 1.15 mmol) 1,2-ethanediol, and 10 mg (0.053 mmol) *p*-TsOH in 25 ml dry benzene was boiled under reflux at a *"Dean-Stark"*-trap for 12 h (Ar-atmosphere). The mixture was quenched with 50 ml satd. $NaHCO_3$-solution and extracted with ether. The crude products (215 mg) were separated by chromatography (20 g silicagel). Elution with hexane/ether 1:1 gave 11 mg (4%) diacetal 7, 143 mg (64%) monoacetal **6**, and 40 mg (22%) starting material **2**.

b) *With 5 mol-equiv. diol.* Treatment of 140 mg (0.778 mmol) diketone **2** with 220 µl (244 mg, 3.95 mmol) 1,2-ethanediol and 8 mg (0.042 mmol) *p*-TsOH as described above gave 81 mg (39%) diacetal 7 and 78 mg (45%) monoacetal **6**.

*Data of 9-methyl-8-oxo-*cis*-decalin-1-*spiro*-2'-(1',3'-dioxolane)* (**6**). M.p. 63°. – IR. (CCl_4): 2980*m*, 2940*s*, 2870*s*, 1710*s*, 1702*s*, 1467*m*, 1457*m*, 1448*m*, 1435*w*, 1412*w*, 1377*m*, 1348*w*, 1335*w*, 1320*w*, 1312*w*, 1280*w*, 1270*w*, 1240*m*, 1207*w*, 1183*s*, 1145*m*, 1108*s*, 1090*m*, 1072*s*, 1055*m*, 1025*m*, 1010*m*, 995*w*, 950*m*, 920*m*, 890*w*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 1.30 (*s*, H_3C–C(9)); 1.0–2.2 (*m*, 11 H); 2.2–2.7 (*m*, 2 H–C(7)); 3.6–4.1 (*m*, 2 H–C(4',5')). – MS.: 224 (18, M^+), 209 (1), 195 (2), 181 (6), 179 (2), 167 (2), 153 (2), 137 (2), 124 (8), 112 (91), 99 (83), *86* (100), 77 (5), 67 (6), 53 (5), 41 (10).

$C_{13}H_{20}O_3$ (224.29) Calc. C 69.61 H 8.99% Found C 69.66 H 8.92

*Data of dispiro[(1',3'-dioxolane)-2,1-(9-methyl-*cis*-decalin)-8,2''-(1'',3''-dioxolane)]* (**7**). M.p. 77°. – IR. (CCl_4): 2960*s*, 2930*s*, 2870*s*, 1470*w*, 1455*w*, 1450*m*, 1375*w*, 1348*w*, 1335*w*, 1305*w*, 1287*w*, 1276*w*, 1255*w*, 1243*w*, 1188*m*, 1175*m*, 1156*m* 1140*m*, 1115*m*, 1090*s*, 1077*s*, 1038*m*, 1015*m*, 986*w*, 950*m*, 933*m*, 922*m*, 910*w*, 882*w*, 865*w*, 845*w*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 1.14 (*s*, H_3C–C(9)); 1.0–2.5 (*m*, 13 H); 3.6–4.2 (*m*, 2 H–C(4',5',4'',5'')). – ^{13}C-NMR. (75.5 MHz, $CDCl_3$, –20°): 18.3 (H_3C–C(9)); 19.2 (C(3)); 22.7 (C(6)); 26.8 (C(5)); 27.2 (C(4)); 32.3 (C(7)); 33.5 (C(2)); 42.6 (C(10)); 48.7 (C(9)); 63.0, 63.6, 64.5 and 65.2 (C(4',5',4'',5'')); 112.4 and 112.6 (C(1,8)). – MS. (DI., 120°): 268 (41, M^+), 239 (6), 225 (31), 223 (21), 207 (7), 196 (4), 181 (4), 168 (15), 153 (14), 139 (8), 125 (4), 112 (24), *99* (100), 86 (27), 77 (7), 73 (4), 67 (4), 55 (10), 41 (8).

$C_{15}H_{24}O_4$ (268.34) Calc. C 67.13 H 9.02% Found C 67.01 H 9.02%

Partial hydrolysis of diacetal **7**. A mixture of 27 mg (0.101 mmol) bis-acetal **7** with 5 ml acetone and 3 mg *p*-TsOH was kept for 3 h at RT., the course of reaction being followed by GC. (160°, 0.35 kg/cm^2). After 3 h, when the ratio of starting material **7** (t_R 3.5 min), monoacetal **6** (t_R 5.1 min), and dione **2** (t_R 5.7 min) was 3:89:8, the reaction was quenched with 20 ml satd. $NaHCO_3$-solution and worked up. Chromatography on silicagel (20 g, hexane/ether 1:1) gave 18 mg (80%) monoacetal **6**.

General procedures for the acetalization of dione **2** *with (2*R*,3*R*)-2,3-butanediol (***8***). – Method A: Removal of water by azeotropic distillation.* A mixture of 1.0 mmol of dione **2**, (2*R*,3*R*)-2,3-butanediol (**8**) (usually 1.1 mmol), and 0.05 mmol acid in 20 ml solvent was heated under reflux at a *"Dean-Stark"*-trap (Ar-atmosphere). The course of the reaction is followed by GC. (135°, 0.30 kg/cm^2). After the consumption of all **2**, or, if no further change is observable, the reaction is quenched with satd. $NaHCO_3$-solution and extracted with ether. The composition of the resulting mixture is determined by GC. (diacetal **11**, t_R 6.4 min, monoacetal **10**, t_R 7.4 min, dione **2**, t_R 7.8 min, monoacetal **9**, t_R 8.2 min), and separated by chromatography on the 100-fold amount of silicagel: elution with hexane/ether 5:1 gives diacetal **11**, monoacetal **10**, monoacetal **9**, and starting material **2**; the ester **17** is eluted with ether/hexane 1:1.

Method B: Removal of water by absorption with molecular sieves. A solution of 1.0 mmol diketone **2** and (2*R*,3*R*)-2,3-butanediol (**8**) (usually 1.2 mmol) in 10 ml dry benzene (or another solvent) is prepared. The temperature, if not RT., is controlled by a thermostated oil-bath, or by a cryostate. The acid-catalyst (*ca.* 0.1 mmol) and 0.5 g molecular sieves (MS, *Union Carbide*, type *5Å*, powder), freshly activated by heating to ≈300° at HV., are then added, and the mixture is stirred under Ar. The reaction mixture is analyzed and separated as described above.

*Data of (9*S*,10*R*)-9-methyl-8-decalone-1-*spiro*-2'-[(4'*R*,5'*R*)-4',5'-dimethyl-1',3'-dioxolane]* (**9**). M.p. 70°, $[\alpha]_D = +20.3°$ ($c = 1.72$, $CHCl_3$). – UV. (EtOH): 296 ($\varepsilon = 33$). – CD. (EtOH): 304 nm ($\Delta\varepsilon \approx 0.916$). – IR. ($CCl_4$): 2970*s*, 2930*s*, 2860*s*, 1710*s*, 1700*s*, 1465*m*, 1450*m*, 1445*m*, 1435*m*, 1410*w*, 1372*m*, 1352*w*, 1335*w*, 1320*w*, 1310*w*, 1288*w*, 1275*m*, 1265*w*, 1239*m*, 1205*w*, 1190*m*, 1166*w*, 1140*m*, 1105*s*, 1095*s*, 1085*s*, 1055*m*, 1045*m*, 1010*w*, 992*w*, 975*w*, 955*m*, 932*m*, 918*m*, 900*w*, 880*w*. – ^{1}H-NMR. (300 MHz, $CDCl_3$): 1.17 and 1.24 (2*d*, $J = 6$ and 6, H_3C–C(4',5')); 1.33 (*s*, H_3C–C(9)); 1.3 – 2.1 (*m*, 11 H); 2.4–2.7 (*m*, 2 H–C(7));

3.36 and 3.69 (2*d* × *qa*, *J* = 9 and 6, for each, H–C(4′,5′)). – ^{13}C-NMR. (25.2 MHz, $CDCl_3$): 16.1, 17.7 and 18.9 (H_3C–C(9,4′,5′); 20.9 (C(6)); 23.9, 26.9 and 27.5 (C(3,4,5)); 33.3 (C(2)); 40.9 (C(7)); 44.8 (C(10)); 56.9 (C(9)); 78.2 and 78.4 (C(4′,5′)); 110.3 (C(1)); 213.3 (C(8)). – MS. (DI., 120°): 252 (10, *M*+), 237 (1), 223 (5), 209 (4), 193 (5), 181 (4), 164 (8), 155 (6), 140 (87), 127 (82), *114* (100), 93 (5), 81 (6), 67 (6), 55 (31), 43 (9), 41 (12).

$C_{15}H_{24}O_3$ (252.34) Calc. C 71.39 H 9.59% Found C 71.21 H 9.63%

*Data of (9*R*,10*S*)-9-methyl-8-decalone-1*-spiro-*2′-[(4′*R*,5′*R*)-4′,5′-dimethyl-1′,3′-dioxolane]* (**10**). $[\alpha]_D = -26.0°$ (*c* = 1.78, $CHCl_3$). – UV. (EtOH): 296 ($\varepsilon \approx 30$). – CD. (EtOH): 304 nm ($\Delta\varepsilon = -0.749$). – IR. ($CCl_4$): 2970*s*, 2930*s*, 2870*s*, 1703*s*, 1465*m*, 1460*m*, 1448*m*, 1415*w*, 1392*w*, 1378*m*, 1339*m*, 1320*w*, 1312*w*, 1290*w*, 1278*m*, 1270*w*, 1241*m*, 1205*w*, 1190*s*, 1170*w*, 1153*m*, 1140*m*, 1100*s*, 1087*s*, 1058*m*, 1052*m*, 1012*w*, 1000*m*, 980*m*, 960*m*, 940*m*, 920*m*, 903*w*, 885*m*, 870*w*, 855*w*, 840*w*. – ^{1}H-NMR. (300 MHz, $CDCl_3$): 1.19 and 1.23 (2*d*, *J* = 6 and 6) (H_3C–C(4′,5′)); 1.32 (*s*, H_3C–C(9)); 1.2–2.1 (*m*, 11 H); 2.2–2.4 and 2.5–2.7 (2 *m*, 2 H–C(7)); 3.41 and 3.60 (2*d* × *qa*, *J* = 8 and 6 for each, H–C(4′,5′)). – ^{13}C-NMR. (75.5 MHz, $CDCl_3$): 16.1, 18.2 and 18.5 (H_3C–C(9,4′,5′)); 21.2 (C(6)); 23.7, 26.5 and 27.4 (C(3,4,5)); 33.3 (C(2)); 40.4 (C(7)); 44.5 (C(10)); 57.0 (C(9)); 76.3 and 79.7 (C(4′,5′)); 110.0 (C(1)); 212.8 (C(8)). – MS. (DI., 120°): 252 (10, *M*+), 237 (1), 224 (2), 223 (3), 209 (3), 193 (4), 181 (3), 164 (7), 155 (3), 140 (80), 127 (79), 124 (4), *114* (100), 93 (5), 81 (7), 67 (7), 55 (35), 43 (14), 41 (16).

$C_{15}H_{24}O_3$ (252.34) Calc. C 71.39 H 9.59% Found C 71.53 H 9.77%

*Data of dispiro[((4′*R*,5′*R*)-4′,5′-dimethyl-1′,3′-dioxolane)-2′,1-(9-methyl-*cis*-decalin)-8,2″-(4″*R*,5″*R*)-4″,5″-dimethyl-1″,3″-dioxolane)]* (**11**). $[\alpha]_D = -36.4°$ (*c* = 2.36, $CHCl_3$). – IR. (CCl_4): 2970*s*, 2930*s*, 2870*s*, 1470*w*, 1450*m*, 1440*m*, 1390*w*, 1375*m*, 1350*w*, 1340*w*, 1305*w*, 1291*m*, 1275*m*, 1255*w*, 1240*w*, 1193*m*, 1182*m*, 1170*m*, 1155*w*, 1140*m*, 1110*s*, 1095*s*, 1060*m*, 1045*m*, 1025*m*, 998*m*, 978*w*, 965*m*, 955*m*, 940*m*, 922*m*, 905*w*, 882*w*, 865*w*, 852*w*, 837*w*. – ^{1}H-NMR. (300 MHz, $CDCl_3$, 25°): 1.0–1.3 (*m*) and 1.22 (*d*, *J* = 6) (H_3C–C(9,4′,5′,4″,5″)); 1.0–2.1 and 2.3–2.6 (2 *m*, 13 H); 3.58 (*d* × *qa*, *J* = 9 and 6) and 3.3 – 3.9 (*m*) (H–C(4′,5′,4″,5″)). – ^{1}H-NMR. (300 MHz, $CDCl_3$, 75°): 1.154 (*s*, H_3C–C(9)); 1.158, 1.163, 1.21 and 1.25 (4 *d*, *J* = 6 for each, H_3C–C(4′,5′,4″,5″)); 1.2–2.0 (*m*, 13 H); 3.57 (*d* × *qa*, *J* = 9 and 6) and 3.4–3.9 (*m*) (H–C(4′,5′,4″,5″)). – ^{13}C-NMR. (75.5 MHz, $CDCl_3$, –20°): 15.6, 15.95, 16.03, 16.2, 17.7, 17.8, 18.0, 18.2, 18.5 and 19.3 (H_3C–C(9,4′,5′,4″,5″)); 18.7/19.4 and 22.7/23.1 (C(3,6)); 26.8, 27.2, 27.38 and 27.43 (C(4,5)); 34.6, 34.9, 35.0 and 36.5 (C(2,7)); 42.2/42.4 (C(10)); 48.4/49.1 (C(9)); 75.9, 76.1, 76.2, 77.8 (2C), 78.0, 78.6 and 79.8 (C(4′,5′,4″,5″)); 110.9, 111.6, 111.7 and 112.1 (C(1,8)). – MS.: 324 (16, *M*+), 309 (1), 281 (12), 269 (6), 265 (7), 253 (31), 251 (20), 235 (2), 227 (4), 209 (4), 195 (5), 181 (11), 167 (9), 152 (4), 140 (16), *127* (100), 114 (29), 95 (4), 81 (8), 73 (5), 69 (6), 67 (6), 55 (30), 45 (2), 43 (11), 41 (11).

*Data of 3‴-hydroxy-2‴-butyl 4-[spiro((4″*R*,5″*R*)-4″,5″-dimethyl-1″,3″-dioxolane)-2″,3′-(2′-methylcyclohexyl)]butanoat* (**17**). – IR. ($CHCl_3$): 3600*m*, 2980*s*, 2940*s*, 2870*m*, 1727*s*, 1460*w*, 1455*m*, 1445*m*, 1378*m*, 1290*w*, 1180*w*, 1167*m*, 1095*s*, 1055*m*, 1040*m*, 1015*w*, 980*w*, 945*w*, 920*w*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 0.75–0.9 and 1.15–1.3 (2 *m*, 3 H–C(1‴,4‴, H_3C–C(2′,4″,5″)); 1.0–2.2 (*m*, 12 H); 1.9–2.1 (*m*, HO); 2.2–2.4 (*m*, 2 H–C(2)); 3.3–3.8 (*m*, H–C(4″,5″,3‴)); 4.74 (*d* × *qa*, *J* = 6 and 6, H–C(2‴)). – MS. (DI., 120°): 342 (15, *M*+), 313 (7), 299 (31), 271 (11), 253 (14), 227 (2), 211 (6), 197 (3), 183 (37), 163 (4), 154 (3), 139 (15), 135 (14), *127* (100), 114 (29), 111 (13), 95 (6), 81 (6), 73 (9), 67 (6), 55 (41), 45 (11), 43 (12), 41 (14).

Experiments with method A. Exper. 1: 466 mg (2.59 mmol) **2**, 257 mg (2.86 mmol) **8**, 15 mg (0.079 mmol) *p*-TsOH · H_2O in 25 ml benzene. Reaction time 18 h, yield: 325 mg (50%) **9**, 100 mg (15%) **10**, and 111 mg (24%) **2** (starting material). Ratio **9/10** = 77:23 (GC.).

Exper. 2: 183 mg (1.02 mmol) **2**, 458 mg (5.09 mmol) **8**, 11 mg (0.058 mmol) *p*-TsOH · H_2O in 20 ml benzene. Reaction time 6 h, yield: 31 mg (9%) **11**, 172 mg (67%) **9**, and 43 mg (17%) **10**, ratio **9/10** = 80:20 (GC.).

Exper. 3: 229 mg (1.27 mmol) **2**, 126 mg (1.4 mmol) **8**, 9 mg (0.047 mmol) *p*-TsOH · H_2O in 25 ml toluene. Reaction time 18 h, yield: 144 mg (45%) **9**, 26 mg (8%) **10**, and 89 mg (39%) **2**, ratio **9/10** = 85:15 (GC).

Exper. 4: 99 mg (0.55 mmol) **2**, 54 mg (0.61 mmol) **8**, 5 mg (0.026 mmol) *p*-TsOH · H_2O in 10 ml CH_2Cl_2. Reaction time 22 h, yield: 4 mg (2%) **11**, 75 mg (54%) **9**, 25 mg (18%) **10**, and 15 mg (15%) **2**, ratio **9/10** = 75:25 (GC.).

Exper. 5: 171 mg (0.95 mmol) **2**, 103 mg (1.14 mmol) **8**, and 12 mg (0.051 mmol) MSA in 20 ml benzene. Reaction time 5 h, yield: 5mg (2%) **11**, 138 mg (58%) **9**, 32 mg (13%) **10**, and 29 mg (17%) **2**, ratio **9/10** = 82:18 (GC.).

Experiments with method B. Exper. 6: 87 mg (0.484 mmol) **2**, 53 mg (0.584 mmol) **8**, 12 mg (0.051 mmol) MSA, and 260 mg molecular sieves (MS) 5A in 5 ml benzene. Temp.: 80° (reflux), reaction time 48 h, yield: 60 mg (49%) **9**, 13 mg (11%) **10**, and 29 mg (33%) **2**, ratio **9/10** = 82:18 (GC.).

Exper. 7: 202 mg (1.12 mmol) **2**, 121 mg (1.34 mmol) **8**, 24 mg (0.102 mmol) MSA, and 570 mg MS (5A) in 10 ml benzene. RT., reaction time 72 h, yield: 19 mg (5%) **11**, 215 mg (76%) **9**, 30 mg (11%) **10**, and 6 mg (3%) **2**, ratio **9/10** = 88:12 (GC.).

Exper. 8: 206 mg (1.14 mmol) **2**, 124 mg (1.38 mmol) **8**, 24 mg (0.102 mmol) MSA and 550 mg MS (5A) in 10 ml benzene. Temp.: –5°, reaction time 108 h, yield: 17 mg (5%) **11**, 214 mg (74%) **9**, 25 mg (9%) **10**, and 16 mg (8%) **2**, ratio **9/10** = 90:10 (GC.).

Exper. 9: 89 mg (0.494 mmol) **2**, 223 mg (2.448 mmol) **8**, 12 mg (0.051 mmol) MSA, and 280 mg MS (5A) in 5 ml benzene. RT., reaction time 60 h, yield: 11 mg (7%) **11**, 89 mg (71%) **9**, 15 mg (12%) **10**, and 4 mg (4%) **2**, ratio **9/10** = 86:14 (GC.).

Exper. 10: 90 mg (0.50 mmol) **2**, 54 mg (0.594 mmol) **8**, 12 mg (0.051 mmol) MSA, and 250 mg MS (5A) in 5 ml cyclohexane. RT., reaction time 120 h (no change was observed after 48 h), yield: 5 mg (3%) **11**, 63 mg (50%) **9**, 13 mg (10%) **10**, and 30 mg (33%) **2**, ratio **9/10** = 84:16 (GC.).

Exper. 11: 92 mg (0.51 mmol) **2**, 56 mg (0.617 mmol) **8**, 24 mg (0.102 mmol) MSA, and 255 mg MS (5A) in 5 ml benzene. RT., reaction time 19 h, yield: 10 mg (6%) **11**, 90 mg (70%) **9**, and 18 mg (14%) **10**, ratio **9/10** = 83:17 (GC.).

Exper. 12: 99 mg (0.55 mmol) **2**, 60 mg (0.66 mmol) **8**, 5 mg (0.021 mmol) MSA, and 270 mg MS (5A) in 5 ml benzene. RT., reaction time 288 h, yield: 56 mg (40%) **9**, 6 mg (4%) **10**, and 48 mg (48%) **2**, ratio **9/10** = 90:10 (GC.).

Exper. 13: A mixture of 12 mg (0.051 mmol) MSA and 280 mg MS (5A) in 3 ml benzene was stirred for 2 days at RT. and under Ar. Addition of 97 mg (0.539 mmol) **2** and 59 mg (0.65 mmol) **8**. RT., reaction time 72 h, yield: 5 mg (3%) **11**, 103 mg (76%) **9**, 13 mg (10%) **10**, and 6 mg (6%) **2**, ratio **9/10** = 89:11 (GC.).

Exper. 14: 93 mg (0.52 mmol) **2**, 56 mg (0.617 mmol) **8**, 23 mg (0.094 mmol) 2-naphtalenesulfonic acid·$2H_2O$, and 260 mg MS (5A) in 5 ml benzene. RT., reaction time 8 h, yield: 12 mg (7%) **11**, 77 mg (59%) **9**, 24 mg (18%) **10**, and 2 mg (2%) **2**, ratio **9/10** = 76:24 (GC.).

Exper. 15: 84 mg (0.466 mmol) **2**, 51 mg (0.562 mmol) **8**, 11 mg (0.045 mmol) 2-naphtalenesulfonic acid·$2H_2O$, and 260 mg MS (5A) in 5 ml benzene. RT., reaction time 27 h, yield: 2 mg (1%) **11**, 81 mg (69%) **9**, 19 mg (16%) **10**, and 6 mg (7%) **2**, ratio **9/10** = 81:19 (GC.).

Exper. 16: 103 mg (0.572 mmol) **2**, 62 mg (0.683 mmol) **8**, 17 mg (0.06 mmol) 2,4,6-triisopropylbenzenesulfonic acid, and 285 mg MS (5A) in 5 ml benzene. RT., reaction time 72 h, yield: 10 mg (5%) **11**, 106 mg (74%) **9**, 12 mg (8%) **10**, and 7 mg (7%) **2**, ratio **9/10** = 90:10 (GC.).

Exper. 17: 89 mg (0.494 mmol) **2**, 54 mg (0.595 mmol) **8** 10 mg (0.053 mmol) *p*-TsOH·H_2O, and 260 mg MS (5A) in 5 ml benzene. RT., reaction time 22 h, yield: 8 mg (5%) **11**, 88 mg (71%) **9**, 21 mg (17%) **10**, and 2 mg (2%) **2**, ratio **9/10** = 81:19 (GC.).

Exper. 18: 90 mg (0.50 mmol) **2**, 54 mg (0.595 mmol) **8**, 10 mg (0.053 mmol) 4-methoxybenzenesulfonic acid, and 265 mg MS (5A) in 5 ml benzene. RT., reaction time 24 h, yield: 8 mg (5%) **11**, 89 mg (71%) **9**, and 21 mg (17%) **10**, ratio **9/10** = 81:19 (GC.).

Exper. 19: 93 mg (0.517 mmol) **2**, 56 mg (0.617 mmol) **8**, 4 μl (6 mg, 0.062 mmol) CH_3SO_3H, and 270 mg MS (5A) in 5 ml benzene. RT., reaction time 22 h, yield: 8 mg (5%) **11**, 88 mg (68%) **9**, 22 mg (17%) **10**, and 2 mg (2%) **2**, ratio **9/10** = 80:20 (GC.).

Exper. 20: 93 mg (0.517 mmol) **2**, 56 mg (0.626 mmol) **8**, 5 μl (*ca.* 0.056 mmol) trifluoromethanesulfonic acid, and 270 mg MS (5A) in 5 ml benzene. RT., reaction time 6 h, yield: 14 mg (8%) **11**, 45 mg (35%) **9**, 26 mg (20%) **10**, 15 mg (16%) **2**, and 32 mg (18%) **17**, ratio **9/10** = 63:37 (GC.).

Exper. 21: 90 mg (0.50 mmol) **2**, 55 mg (0.605 mmol) **8**, 20 mg *Amberlyst-15* (H^+), and 270 mg MS (5A) in 5 ml benzene. RT., reaction time 120 h, yield: 4 mg (2%) **11**, 34 mg (27%) **9**, 11 mg (9%) **10**, 22 mg (24%) **2**, and 57 mg (33%) **17**, ratio **9/10** = 76:24 (GC.).

Transformation of monoacetal **9** *into (+)-(9*R,*10*R*)-9-methyl-1-decalone* ((+)-**12**). – a) *Preparation of (9*S,*10*R*)-9-methyl-8-tolylsulfonylhydrazono-decalin-1*-spiro-*2'-[(4'*R,*5'*R*)-4',5'-dimethyl-1',3'-dioxolane]* (**13**). A solution of 90 mg (0.357 mmol) monoacetal **9** and 80 mg (0.430 mmol) toluenesulfonylhydrazide in 6 ml abs. EtOH was heated under reflux for 18 h (Ar-atmosphere). After evaporation of the solvent, the residue was purified by chromatography on 10 g silicagel. Elution with hexane/ether 1:1 gave 108 mg (72%) **13**. M.p. 158° (CH_3OH), $[\alpha]_D = +54.2°$ ($c = 1.77$, $CHCl_3$). – IR. ($CHCl_3$): 3300*w*, 3210*w*, 2930*s*, 2870*s*, 1597*m*, 1490*w*, 1447*m*, 1377*m*, 1332*m*, 1305*w*, 1288*w*, 1160*s*, 1110*s*, 1090*s*, 1050*w*, 1010*m*, 975*w*,

965*w*, 920*m*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 0.81 and 1.04 (2*d*, *J*=6 and 6, H_3C–C(4′,5′)); 1.33 (*s*, H_3C–C(9)); 0.7–2.8 (*m*, 13 H); 2.39 (*s*, H_3C–$C_6H_4SO_2NHN$=C(8)); 3.2–3.6 (*m*, H–C(4′,5′)); 7.2–7.4 and 7.8–8.0 (2*m*, H_3C–$C_6H_4SO_2NHN$=C(8)); 7.5 (*m*, H_3C–$C_6H_4SO_2NHN$=C(8)). – MS. (DI., 120°): 420 (0.5, M^+), *265* (100), 248 (14), 236 (6), 221 (3), 206 (5), 193 (25), 176 (9), 164 (7), 156 (10), 139 (6), 133 (5), 127 (12), 121 (8), 114 (17), 107 (10), 93 (12), 91 (24), 81 (7), 79 (10), 65 (9), 55 (20), 43 (9), 41 (10).

*b) Preparation of (9*R*,10*R*)-9-methyl-decalin-1-*spiro*-2′-[(4′*R*,5′*R*)-4′,5′-dimethyl-1′,3′-dioxolane]* (**15**). To a solution of 53 mg (0.126 mmol) **13** in 6 ml dry $CHCl_3$ cooled to –14° 16 µl (*ca.* 18 mg, 0.15 mmol) 1,3,2-benzodioxaborole were added by syringe (Ar-atmosphere). After stirring for 45 min at –14°, the reaction was quenched by adding 75 mg (0.551 mmol) $NaOAc \cdot 3H_2O$ followed by heating under reflux for 1 h. The mixture was then filtered through *Celite*, the filter-cake was washed with CH_2Cl_2, and the filtrate evaporated. Chromatography of the crude product on 10 g silicagel eluting with hexane/ether 5:1 gave 26 mg (86%) **15**. $[\alpha]_D$ = –23.3° (*c*=0.92, $CHCl_3$). – IR. ($CHCl_3$): 2970*m*, 2930*s*, 2860*s*, 1465*m*, 1440*m*, 1373*m*, 1338*m*, 1295*w*, 1287*w*, 1277*m*, 1250*w*, 1188*m*, 1161*m*, 1137*s*, 1090*s*, 1035*m*, 1025*m*, 973*m*, 957*m*, 915*m*, 885*m*, 857*w*, 835*w*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 1.00 (*s*, H_3C–C(9)); 1.20 and 1.21 (2*d*, *J*=6 and 6, H_3C–C(4′,5′)); 0.7–1.8 (*m*, 15 H); 3.48 and 3.64 (2*d*×*qa*, *J*=9 and 6 for each, H–C(4′,5′)). – MS.: 238 (11, M^+), 223 (2), 195 (69), 179 (4), 141 (12), *127* (100), 114 (28), 95 (7), 81 (8), 67 (8), 55 (25), 43 (6), 41 (9).

c) *Preparation of (+)-(9*R*,10*R*)-9-methyl-1-decalone* ((+)**12**). A solution of 22 mg (0.092 mmol) acetal **15** in 2 ml EtOH/1N HCl 5:1 was stirred for 12 h at RT. After treating with 20 ml satd. $NaHCO_3$-solution and working up by extraction with ether, the crude product (15 mg) was purified by chromatography on 10 g silicagel. Elution with hexane/ether 5:1 gave 13 mg (85%) **12**, which was further purified by „Kugelrohr"-distillation. $[\alpha]_D$ = +30.5° (*c*=0.40, $CHCl_3$). – IR. (CCl_4): 2980*m*, 2940*s*, 2870*m*, 1708*s*, 1467*m*, 1460*m*, 1445*m*, 1422*m*, 1378*m*, 1347*w*, 1337*w*, 1315*m*, 1273*w*, 1238*m*, 1145*m*, 1103*m*, 1038*w*, 1020*w*, 992*m*, 945*w*, 920*w*, 880*w*. – ^{1}H-NMR. (80 MHz, $CDCl_3$): 1.21 (*s*, H_3C–C(9)); 0.7–2.8 (*m*, 15 H). – MS.: 166 (23, M^+), 151 (16), 148 (7), 137 (5), 133 (7), 124 (58), 122 (21), *111* (100), 109 (19), 95 (60), 84 (14), 81 (51), 79 (12), 67 (44), 55 (26), 41 (37).

Transformation of monoacetal **10** *into (–)-(9*S*,10*S*)-9-methyl-1-decalone* ((–)**12**): a) *Preparation of (9*R*,10*S*)-9-methyl-8-tolylsulfonylhydrazono-decalin-1-*spiro*-2′-[(4′*R*,5′*R*)-4′,5′-dimethyl-1′,3′-dioxolane]* (**14**). After treating 85 mg (0.337 mmol) **10** with 78 mg (0.419 mmol) toluenesulfonylhydrazide as described above for **9**, chromatography gave 112 mg (79%) **14**. M.p. 163–164° (dec.), $[\alpha]_D$ = –68.4° (*c*=1.83, $CHCl_3$). – IR. ($CHCl_3$): 3310*w*, 2970*m*, 2940*m*, 2880*m*, 1602*w*, 1495*w*, 1450*m*, 1380*m*, 1335*m*, 1308*w*, 1290*w*, 1188*w*, 1167*s*, 1145*w*, 1112*m*, 1093*s*, 1057*w*, 1018*m*, 982*w*, 968*w*, 917*m*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 0.72 and 1.11 (2*d*, *J*=6 and 6, H_3C–C(4′,5′)); 1.26 (*s*, H_3C–C(9)); 0.9–2.8 (*m*, 13 H); 2.38 (*s*, H_3C–$C_6H_4SO_2NHN$=C(8)); 2.8–3.2 and 3.2–3.6 (2*m*, H–C(4′,5′)); 7.0–7.5 (*m*, H_3C–$C_6H_4SO_2NHN$=C(8)); 7.1–7.4 and 7.8–8.0 (2*m*, H_3C–$C_6H_4SO_2NHN$=C(8)). – MS. (DI., 160°): 421 (0.6, M^++1), 420 (0.3, M^+), *265* (100), 250 (4), 248 (7), 236 (15), 221 (14), 211 (3), 206 (6), 193 (43), 181 (6), 176 (10), 163 (4), 156 (7), 148 (7), 146 (7), 139 (7), 135 (8), 131 (6), 127 (21), 121 (13), 114 (19), 107 (14), 91 (45), 79 (19), 65 (16), 55 (26), 43 (12), 41 (20).

b) *Preparation of (9*S*,10*S*)-9-methyl-decalin-1-spiro-2′-[(4′*R*,5′*R*)-4′,5′-dimethyl-1′,3′-dioxolane]* (**16**). After treating 68 mg (0.162 mmol) of **14** with 20 µl (*ca.* 22 mg, 0.192 mmol) 1,3,2-benzodioxoborole as described above for **13**, 100 mg (0.735 mmol) $NaOAc \cdot 3H_2O$ were added, and the mixture was heated under reflux for 2 h. Workup and purification as above gave 29 mg (75%) of **16**. $[\alpha]_D$ = –3.4° (*c*=1.25, $CHCl_3$). – IR. ($CHCl_3$): 2970*m*, 2930*s*, 2860*s*, 1466*m*, 1442*m*, 1375*m*, 1335*w*, 1295*w*, 1287*w*, 1278*w*, 1270*w*, 1250*w*, 1193*w*, 1165*m*, 1132*m*, 1110*m*, 1093*s*, 1038*w*, 1025*m*, 1019*m*, 990*w*, 972*m*, 962*w*, 952*m*, 917*m*, 888*m*, 858*w*, 832*w*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 0.99 (*s*, H_3C–C(9)); 1.18 and 1,23 (2 *d*, *J*=6 and 6, H_3C–C(4′,5′)); 0.8–2.0 (*m*, 15 H); 3.46 and 3.64 (2*d*×*qa*, *J*=9 and 6 for each, H–C(4′,5′)). – MS.: 238 (10, M^+), 223 (2), 195 (64), 179 (5), 148 (5), 141 (14), *127* (100), 122 (7), 114 (34), 95 (9), 81 (10), 67 (12), 55 (34), 53 (5), 43 (10), 41 (17).

c) *Preparation of (–)-(9*S*,10*S*)-9-methyl-1-decalone ((–)-***12***).* Hydrolysis starting from 20 mg (0.084 mmol) of **16** was carried out as described above for **15**. Yield: 12 mg (86%) (–)-**12**. $[\alpha]_D$ = –30.7° (*c*=0.45, $CHCl_3$). – IR., ^{1}H-NMR., and MS. see above for (+)-**12**.

Acetalization of monoacetal **9**. A mixture of 50 mg (0.198 mmol) monoacetal **9**, 36 mg (0.396 mmol) diol **8**, 12 mg (0.051 mmol) MSA, and 210 mg MS (5A) in 5 ml benzene was treated according to method B. The reaction was quenched after 12 days and worked up as usual. Yield: 14 mg (22%) diacetal **11** and 37 mg (74%) **9** (starting material).

Acetalization of monoacetal **10**. A mixture of 56 mg (0.222 mmol) of **10**, 40 mg (0.441 mmol) of **8**,

12 mg (0.051 mmol) MSA, and 250 mg MS (5A) in 5 ml benzene was treated according to method B. After 7 days of reaction 45 mg (62%) diacetal **11** and 18 mg (32%) **10** (starting material) were isolated.

Acetalization of dione **2** *by transacetalization.* a) *With (4*R,5R*)-2-ethyl-2,4,5-trimethyl-1,3,dioxolane* (**18**). A solution of 91 mg (0.506 mmol) **2**, 144 mg (1.00 mmol) **18**, *ca.* 4 mg (2*R*,3*R*)-2,3-butanediol (**8**), and 5 mg (0.026 mmol) *p*-TsOH·H_2O in 5 ml benzene was stirred under Ar at RT. The mixture was analyzed by GC. (135°, 0.30 kg/cm^2) after 16, 26, 42, 50, 73, 122, and 145 h. Usual workup after 168 h and chromatographic separation gave 26 mg (20%) **9**, 12 mg (12%) **10**, 35 mg (39%) **2** (starting material), and 30 mg (17%) **17**. Ratio **9**/**10** = 69:31 (GC.).

b) *With (2*R,3R*)-2,3-dimethyl-1,4-dioxaspiro[4.4]nonane* (**19**). A solution of 90 mg (0.50 mmol) **2** in 5 ml benzene was treated as above with 156 mg (1.00 mmol) **19**, *ca.* 3 mg **8**, and 5 mg (0.026 mmol) *p*-TsOH·H_2O for 216 h. Samples were analyzed by GC. after 2.5, 17, 26, 40, 50, 64, 74, 136, 161, 208, and 216 h. Column chromatography gave 31 mg (25%) **9**, 14 mg (11%) **10**, and 37 mg (41%) **2**, ratio **9**/**10** = 69:31 (GC.).

*Acetalization of 9-methyl-*trans*-decalin-1,8-dione* (**3**). – *Method A.* After treating for 14 h 224 mg (1.245 mmol) of **3** with 168 mg (1.87 mmol) of **8** and 20 mg (0.105 mmol) *p*-TsOH·H_2O in 30 ml benzene according to method A, usual workup and purification by column chromatography gave 265 mg (84%) of **20** and **21**, ratio **20**/**21** = 52:48 (determined by ^{1}H-NMR., *vide infra*).

Method B. A mixture of 189 mg (1.05 mmol) of **3**, 114 mg (1.266 mmol) of **8**, 24 mg (0.102 mmol) MSA, and 510 mg MS (5A) in 10 ml benzene was reacted for 48 h at RT. and yielded 246 mg (93%) **20** + **21**, ratio **20**/**21** = 52:48 (determined by ^{1}H-NMR.).

*Data of (9*R,*10*R*)- and (9*S,*10*S*)-9-methyl-8-decalone-1-*spiro*-2'-[(4'*R,*5'*R*)-4',5'-dimethyl-1'3'-dioxolane]* (**20** and **21** resp.). – IR. (CCl_4): 2930*s*, 2870*s*, 1712*s*, 1460*m*, 1450*m*, 1440*m*, 1425*w*, 1375*m*, 1338*w*, 1315*w*, 1288*m*, 1267*m*, 1245*w*, 1235*w*, 1199*m*, 1183*m*, 1160*m*, 1152*m*, 1126*m*, 1110*m*, 1095*s*, 1045*m*, 1020*w*, 1005*w*, 980*m*, 965*m*, 932*m*, 900*w*, 875*w*. – ^{1}H-NMR. (300 MHz, $CDCl_3$): 1.19 (*d*, *J* = 6, 6 H), 1.225 (*d*, *J* = 6), 1.225 (*s*), 1.23 (*s*) and 1.33 (*d*, *J* = 6) (H_3C–C(9,4',5')); 1.3–2.0 (*m*, 10 H); 2.1–2.6 (*m*, 3 H); 3.66 and 4.02 (2d × *qa*, *J* = 8.5 and 6 for each, H–C(4',5') of **20**); 3.745 and 3.90 (2*d* × *qa*, *J* = 8.5 and 6 for each, H–C(4',5') of **21**). – MS.: 252 (15, M^+), 237 (1), 223 (4), 209 (3), 193 (3), 181 (13), 170 (4), 164 (9), 155 (7), 140 (77), 127 (79), *114* (100), 93 (5), 81 (8), 67 (8), 55 (27), 53 (7), 43 (16), 41 (19).

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