16. Investigations Concerning an Unexpected Reaction between the Dimsyl Anion (= (Methylsulfinyl)methanide) and a γ,δ-Epoxy-ketone

by **René Beerli**[1]) and **Hans-Jürg Borschberg***

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Universitätstrasse 16, CH–8092 Zürich

(10.XII.91)

The reaction of 2,2-dimethyl-5-(1,2-epoxypropyl)cyclohexanone (**7**) with *t*-BuOK in DMSO furnished a small amount of 5-(1-hydroxyprop-2-enyl)-2,2-dimethylcyclohexanone (**12**) and the 4 unexpected products **13**–**16** which contain one to three additional C-atoms (*Scheme 2*). The relative configuration of the major product 1-(4′,4′-dimethyl-2′,3′-dimethylidenecyclohexyl)propane-1,2-diol (**15**) was shown to be 1*RS*,2*RS*,1′*SR via* NOE measurements performed on a derivative thereof. A crossover experiment in DMSO/[$^{13}C_2$]DMSO 1:1 as solvent showed that the two additional C-atoms of this product originate from a single molecule of DMSO (*Scheme 5*). A tentative mechanistic scheme, consistent with all experimental observations, is proposed which involves a [2,3]-sigmatropic rearrangement of an (allylsulfinyl)methanide to a sulfenic acid as one of the key steps (**V** → **24**, *Scheme 8*). We corroborated part of this hypothetic scheme by taking recourse to a model compound (7-(methylsulfinyl)-*p*-mentha-1,8-diene (**32**/**33**), readily prepared in two steps from perilla alcohol (**30**)), which reacted as predicted by the proposed mechanism (*Schemes 9* and *10*).

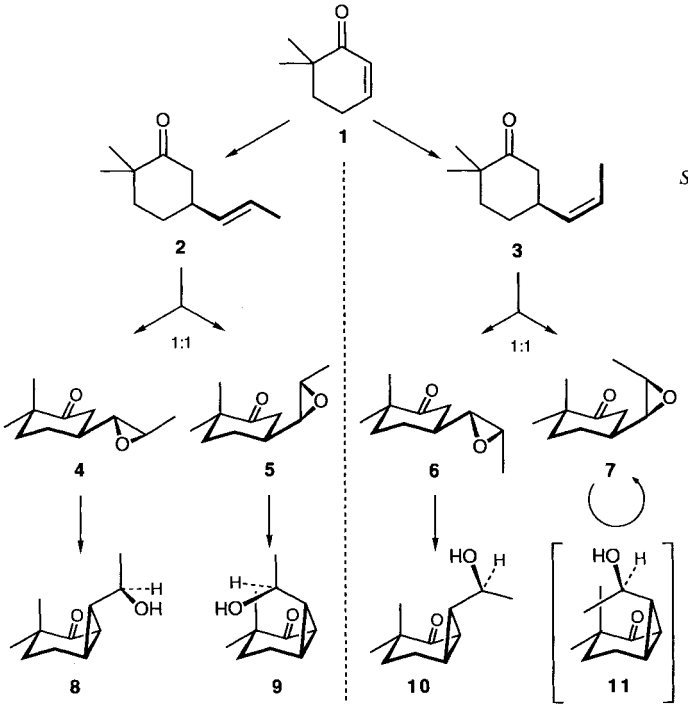
1. Introduction. – In the course of an investigation on the stereochemical outcome of the reductive fragmentation of 'cyclopropylogous'[2]) α-haloketones, the two racemic propenylcyclohexanones **2** and **3** (*Scheme 1*) were prepared some time ago from **1** [1]. Treatment of these compounds with 3-chloroperbenzoic acid furnished unseparable 1:1 mixtures of the diastereoisomeric epoxyketone pairs **4**/**5** and **6**/**7**, respectively. Subsequent treatment of **4**/**5** with *t*-BuOK in *t*-BuOH [2] led to the expected mixture of the alkylation products **8** and **9** which were separated by column chromatography [1]. However, when the pair **6**/**7** was subjected to the same treatment, the reaction stopped after consumption of one half of the starting material. An analysis of the mixture formed showed that it consisted of 50% of the *'exo'*-alkylation product **10** and of 50% of one of the starting epoxyketones, now present as a *single* diastereoisomer. Since the cyclization product **10** can only originate from **6**, the unreactive epoxyketone must have the relative configuration **7**[3]) [1].

In an alternative attempt to prepare compound **11**, we later treated pure epoxyketone **7** with *t*-BuOK in DMSO. Under these conditions, the starting material rapidly disappeared and a mixture of compounds was formed. The major product (20–40% yield)

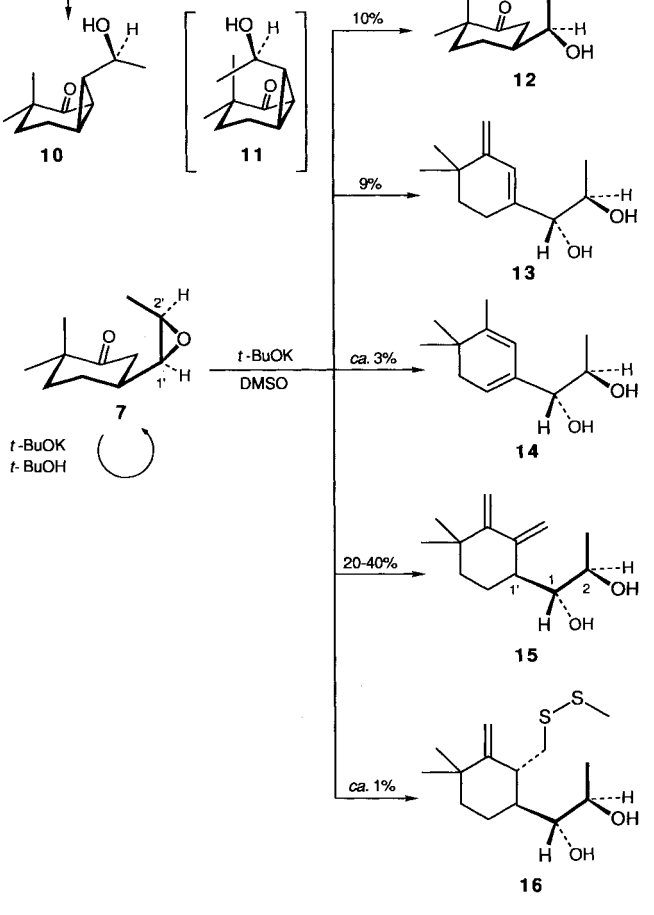
[1]) Taken from a forthcoming thesis of *R. B.*; presented at the autumn meeting of the Swiss Chemical Society, Berne, October 18, 1991.

[2]) This term was coined with the intention to point out the analogy to the well-established notation 'vinylogous' [1].

[3]) An inspection of molecular models suggests that the transition state leading from **7** to the elusive *'endo'*-product **11** would be destabilized through severe nonbonded steric interactions.



Scheme 1



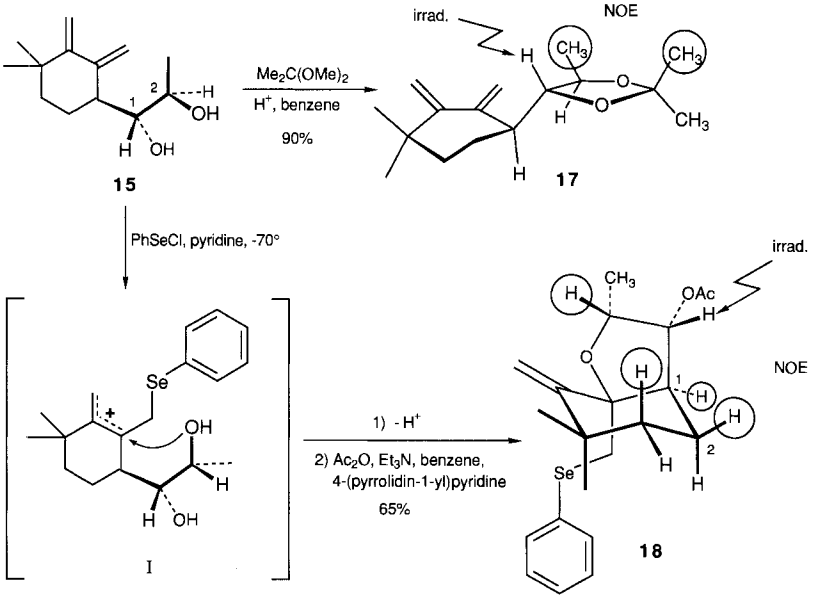
Scheme 2

was isolated and shown to possess the constitutional formula **15** (*Scheme 2*) [3]. We then decided to take a closer look at this unexpected reaction and now present the results of these subsequent investigations.

2. Isolation of the Products and Determination of Their Relative Configuration. – Column chromatography of the mixture obtained from the reaction of **7** with *t*-BuOK in DMSO resulted in the isolation of the three pure products **12**, **15**, and **16** as well as of a 3:1 mixture[4]) of the isomers **13** and **14**.

The major component **15** has a molecular weight of 210 (MS) and the elemental composition $C_{13}H_{22}O_2$ (combustion analysis). While its constitutional formula was readily deduced from its ^{1}H- and ^{13}C-NMR spectra, the determination of the relative configuration of the three adjacent asymmetric centers presented some problems. First it was demonstrated that the arrangement of the two OH groups is of the *'threo'*-type by taking recourse to NOE measurements of the readily prepared cyclic acetal **17** (*Scheme 3*). This

Scheme 3



amounts to a formal *trans*-addition of the two O-functional groups to a (*Z*)-olefin, *i.e.* to an epoxide opening with inversion, as one would expect. To answer the less trivial question, which of the two centers of the epoxy group had been attacked, it was necessary to form an additional bond between the side chain and the six-membered ring. For that reason, **15** was treated with benzeneselenenyl chloride and the crude product acetylated, whereupon the cyclic ether **18** was isolated as the only product. Obviously, the intermediate allylic cation **I** is quenched by the distal OH group (for a review, see [6]) through a

[4]) The composition depends critically on the raction conditions; longer reaction times led to complete equilibration of **13** and **14** [4], favoring the thermodynamically more stable endocyclic isomer **14** (for a review on base-catalyzed isomerizations of olefins, see [5]).

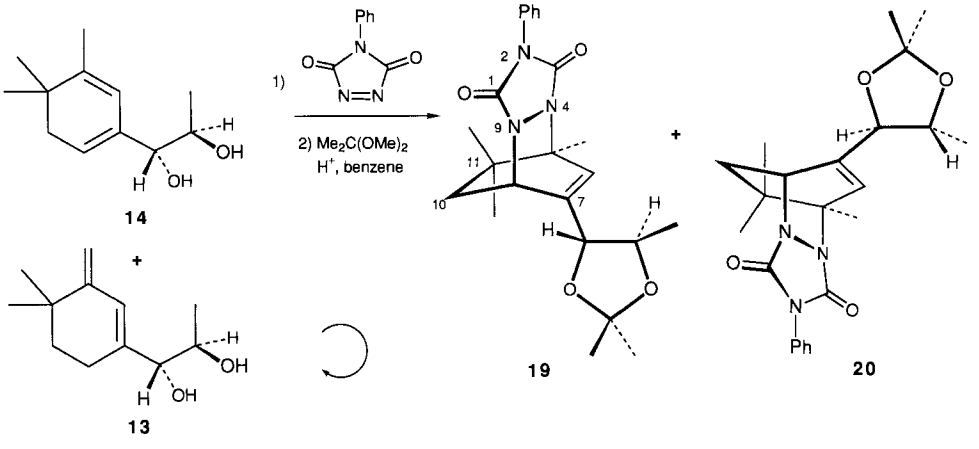
(favored) 5-*exo-trig* pathway [7]. With the aid of NOE measurements, it was possible to deduce the relative configuration of the three asymmetric centers of **18**. A comparison of the configuration of the starting epoxyketone **7** with the one of product **15** shows that – contrary to what one would expect on purely steric grounds – the center next to the ring (C(1′) of **7**) had been attacked with inversion of configuration.

The structure of the minor product **16** was established by its spectral data and comparison with **7** and **15**. For mechanistic reasons (see below), the relative configuration of **16** is assumed to be the same as in **15**.

The MS of **16** has an M^+ region indicative of the presence of 14 C- and 2 S-atoms. The three extra C-atoms turn up as an exocyclic methylidene group, a MeS group (*s* (3H) at 2.45 ppm) which is readily lost in the MS ($[M-47]^+$ at *m/z* 243, see *Scheme 6*), and as a CH_2S unit which appears as *AB* part of an *ABX* system in the ^{1}H-NMR spectrum ($\delta(A) = 3.17$, $\delta(B) = 3.09$, $\delta(X) = 2.81$ ppm; $J_{AB} = 13.1$, $J_{AX} = 4.6$, $J_{BX} = 6.6$ Hz). Furthermore, in the signal of H_X, two long-range couplings with the methylidene protons and an additional vicinal coupling constant of 9.9 Hz can be discerned. Therefore, it is in an allylic position, and both side chains of the cyclohexane ring are equatorially oriented.

The mixture **13**/**14**, which contain one more C-atom than the starting material **7**, was analyzed after a chemical separation: on treatment with the potent dienophile 4-phenyl-3*H*-1,2,4-triazol-3,5(4*H*)-dione [8], the major compound **13** did not react, while the minor component was transformed into a mixture of the two expected *Diels-Alder* adducts which were separated in the form of their cyclic acetal derivatives **19** and **20**[5]) (*Scheme 4*).

Scheme 4

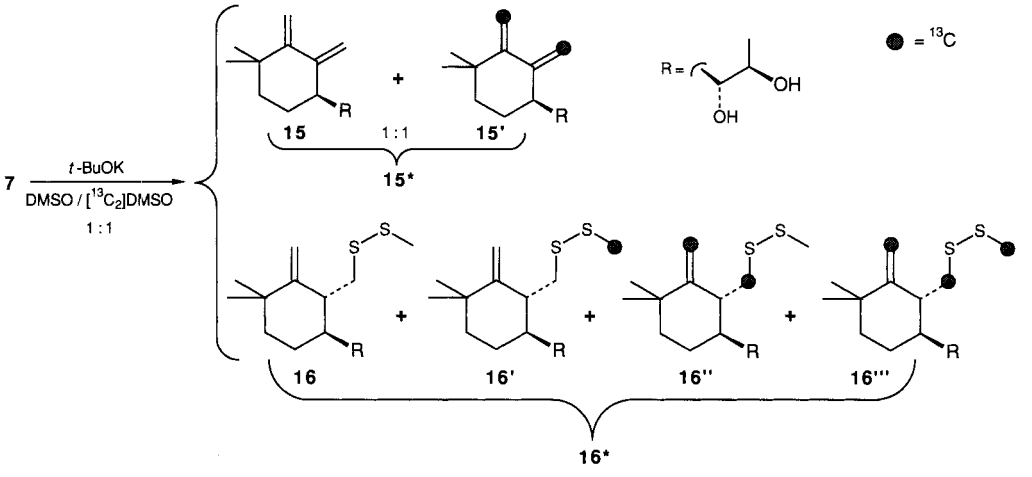


3. Crossover Experiment. – Since the additional C-atoms in the products **13**–**16** most probably originated from the solvent, we prepared a doubly labelled sample of [$^{13}C_2$]DMSO [9]. When **7** was treated with *t*-BuOK in a 1.18:1 mixture [$^{12}C_2$]DMSO/[$^{13}C_2$]DMSO, the usual array of products was obtained, of which **15*** and **16*** were analyzed. In the broad-band ^{1}H-decoupled ^{13}C-NMR spectrum of **15***, only the signals of the two methylidene C-atoms were clearly discernible (111.4 and 106.9 ppm). The fact

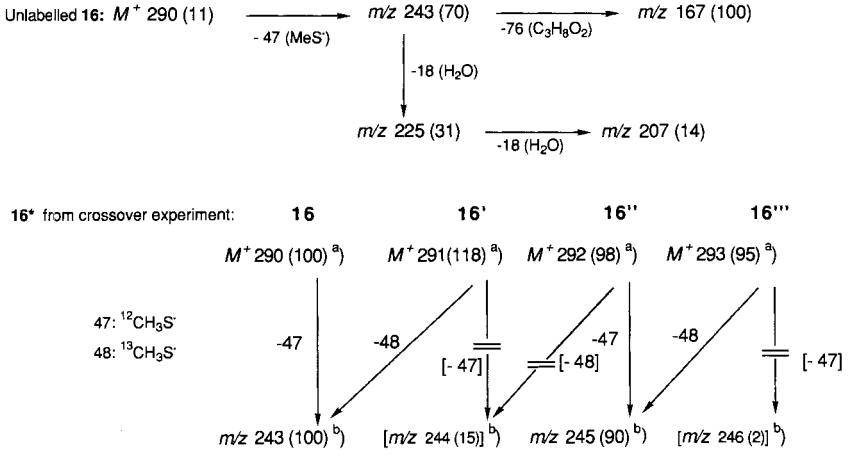
[5]) While the constitution of these two adducts followed readily from their NMR spectra, it was not possible to determine which is which. However, this has no bearing on the deduction of the structure of **14**.

that these signals appear as *d*'s ($^3J(^{13}C,^{13}C) = 3.4$ Hz)[6]) proves that in the ^{13}C-enriched molecules, both C-atoms originate from the *same* [$^{13}C_2$]DMSO molecule[7]).

Scheme 5



Scheme 6. *MS Fragmentation of Unlabelled* **16** *and* ^{13}C*-Labelled* **16***. Relative intensities corrected for natural abundance of ^{13}C and ^{34}S.



a) Normalized relative intensities, I (m/z 290) = 100. b) Normalized relative intensities, I (m/z 243) = 100.

---

6) A corresponding value of 9.1 Hz was reported for s-*trans*-buta-1,3-diene; for an s-*cis*-arrangement, as in **15***, a smaller value is to be expected (see *e.g.* [10] and ref. cit. therein).

7) If the incorporation of the two extra C-atoms had taken place statistically from separate DMSO molecules, one would have expected two additional *s*'s (arising from the two singly labelled forms of **15**), overlapping with the above *d*'s.

An analysis of the M^+ region in the MS of disulfide **16*** showed it to be a 1:1:1:1 mixture of the unlabelled up to the triply labelled species **16**–**16'''**[8]) (*Scheme 5* and *6*).

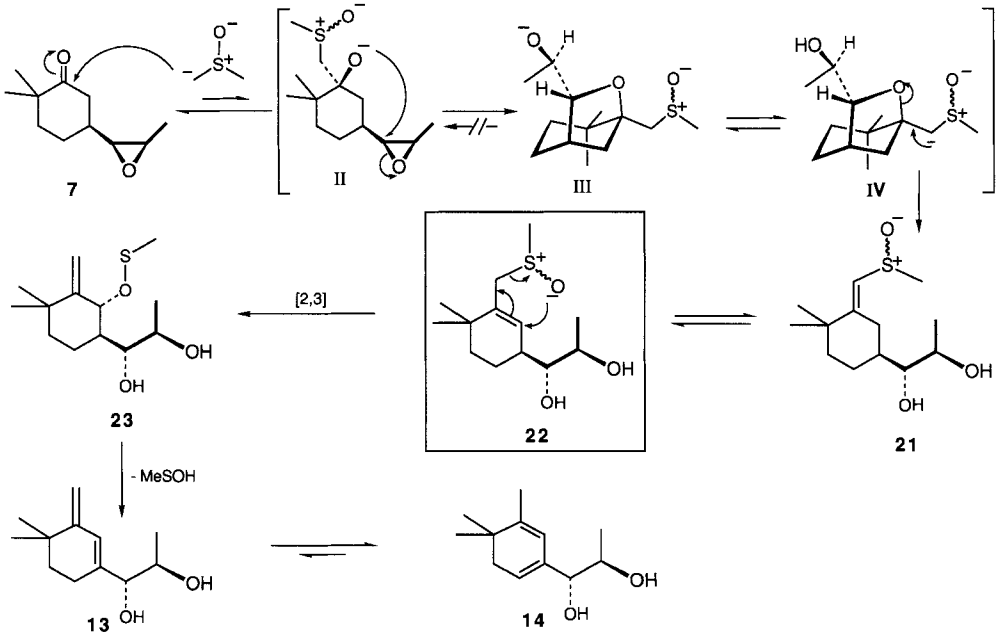
4. Mechanistic Speculations. – A mechanistic scheme that is consistent with the above experimental facts can be summarized as follows:

i) In the major product **15**, both extra C-atoms originate from a *single* molecule of DMSO. The two new C-atoms linked to the cyclohexane ring in disulfide **16** are derived from a single molecule of the solvent, while the third (MeS group) arises from an independent molecule of DMSO.

ii) The opening of the oxirane ring of **7** proceeds with inversion at the center next to the cyclohexane ring.

iii) Control experiments showed that the epoxy function is essential for the formation of the observed products (2,2,5-trimethylcyclohexanone, *e.g.*, undergoes no appearent reaction when treated with *t*-BuOK in DMSO).

Scheme 7



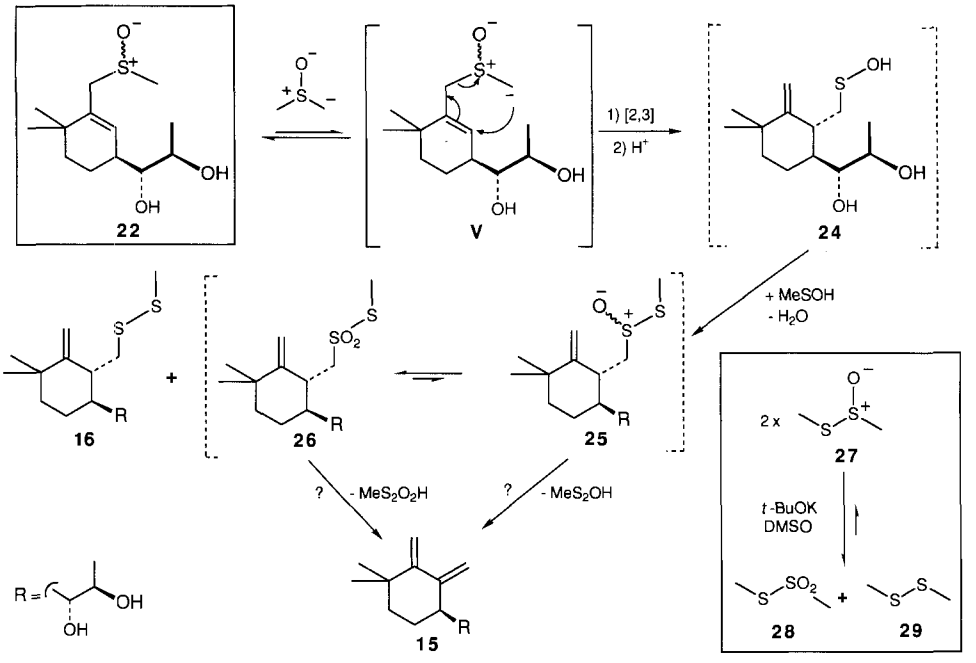
The last two observations can be rationalized as shown in *Scheme 7*: earlier work demonstrated that the ambident dimsyl anion (= (methylsulfinyl)methanide) can attack

[8]) The crucial question where the labelled atoms are located in **16'** and **16''** can be answered by inspection of the $[M - 47/48]^+$ area: the fact that the relative abundance of the ion m/z 244 is very low demonstrates that the parent singly labelled ion M^+ 291 only loses 48 ($^{13}CH_3S^{\cdot}$) to give m/z 243, which means that all ^{13}C-content of the singly labelled species **16'** resides in the *S*-methyl group. A similar reasoning leads to the conclusion that the doubly labelled species **16''** (M^+ 292) loses with preference the fragment 47 ($^{12}CH_3S^{\cdot}$) to give m/z 245 (see *Scheme 6*).

ketones with its C-atom[9]) [12]. In the absence of an oxirane ring, this process is reversible, and the equilibrium probably lies on side of the starting ketone[10]). In the present case, however, the oxirane ring of the corresponding intermediate **II** can be opened by the alkoxide formed in the first step. Thus, the oxirane ring serves as an internal trap for intermediate **II**, because the formed oxolane **III** probably does not revert to **II**. Conceivably, the prototropic form **IV** of this intermediate then undergoes a β-elimination to the α,β-unsaturated sulfoxide **21**, which is in equilibrium with the β,γ-isomer **22** under the prevailing, strongly basic reaction conditions [13].

Appearently, there exist at least two possibilities for the key intermediate **22** to react further: it can undergo a well-documented [2,3]-sigmatropic rearrangement leading to the methanesulfenate **23** (*Scheme 7*; for reviews see [14]). A subsequent base-catalyzed elimination of methanesulfenic acid furnishes the C_1-homologue **13** and finally **14**. As an alternative, **22** is deprotonated to give **V** (*Scheme 8*) which can (at least in principle) undergo a competitive [2,3]-sigmatropic rearrangement that would lead to **24**. This process formes a new C–C bond[11]). The sulfenic acid **24** is not stable under the prevailing

Scheme 8



[9]) An O-attack was postulated by *Comer* and *Temple* [11] to explain the formation of an unexpected product generated during the reaction of the dimsyl anion with cyclopentanone.

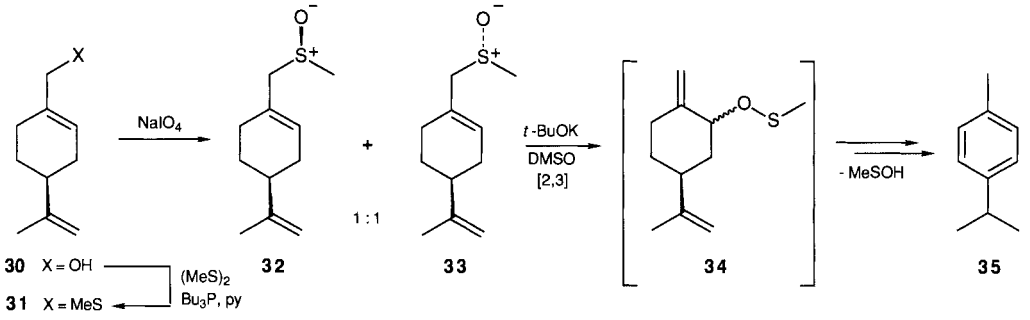
[10]) The corresponding adduct (mixture of diastereoisomers) could be isolated, when [(4-tolyl)sulfinyl]methanide was allowed to react with α-tetralone [12e].

[11]) While there is ample precedent for this type of rearrangement in the case of allylsulfonium ylids (for a review see [15]), we are not aware of analogous cases involving an (allylsulfinyl)methanide.

conditions and reacts with methanesulfenic acid (formed during the step **23** → **13**) to give the *S*-methyl thiosulfinate **25** [16]. Substrates containing this type of functional group are rather unstable and can disproportionate into disulfides and *S*-methyl thiosulfonates[12]) [17]. In the present case, such a process would lead to formation of **16** and **26**. Presently we do not know at which oxidation level of the S-containing side chain the subsequent elimination reaction[13]) to the major product **15** occurs.

To provide more than just circumstancial evidence for the crucial rearrangement step **V** → **24**, we prepared the allyl sulfoxide mixture **32**/**33** as shown in *Scheme 9*: Commercially available (*S*)-perilla alcohol (**30**) was transformed into thio-ether **31** by application of *Nakagawa* and *Hata*'s protocol [18]. Oxidation of **31** with $NaIO_4$ [19] furnished a 1:1 mixture of the sulfoxides **32** and **33**.

Scheme 9



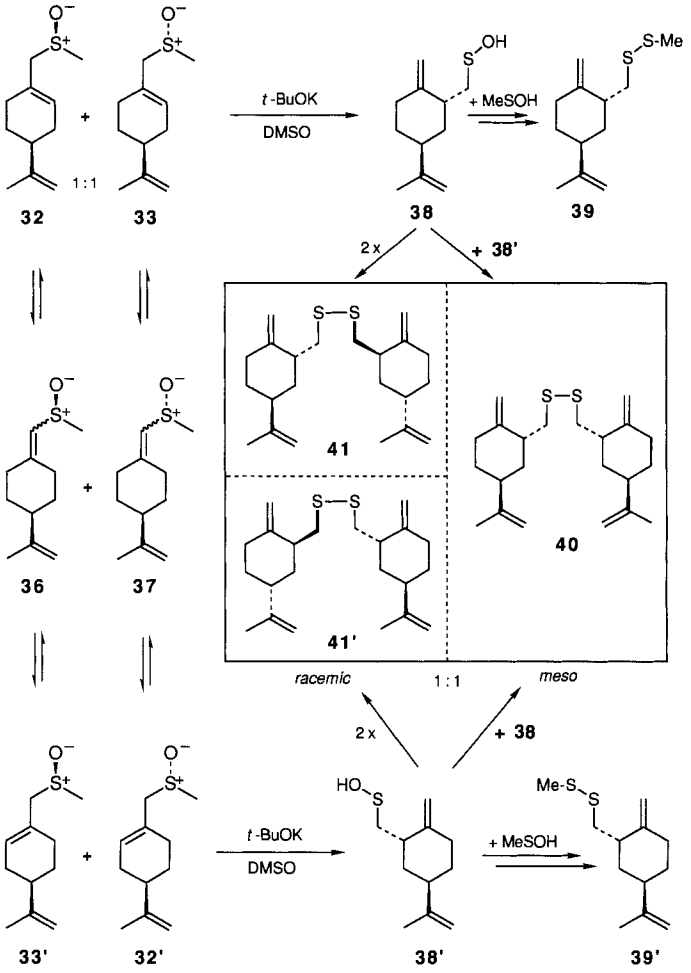
On treatment of the sulfoxides **32**/**33** with *t*-BuOK in DMSO as above, again a mixture of products was obtained: the most volatile component was shown to be *p*-cymene (**35**), which is probably formed by a [2,3]-sigmatropic rearrangement *via* **34** (*Scheme 9*). The major product (27% yield) turned out to be an unseparable 1:1 mixture of the symmetrical disulfides **40** and (±)-**41** (= **41**/**41′**; *Scheme 10*)[14]). In addition, an unsymmetrical disulfide was isolated (6.4% yield) which showed only a very small optical rotation; it is considered to be a nearly racemic mixture of the enatiomers **39** and **39′**. Obviously, the starting components **32** and **33** racemize to **32′** and **33′** (most likely *via* the α,β-unsaturated sulfoxides **36** and **37**, resp.), before they rearrange to the enantiomeric sulfenic acids **38** and **38′**, respectively. The latter dimerize statistically to give the observed mixture of the racemate **41**/**41′** and of the *meso*-compound **40**. In contrast to the system

[12]) Control experiments showed that *S*-methyl methanethiosulfinate (**27**) [17] is stable for several days when kept in neat DMSO at r.t. In the presence of catalytic amounts of base, however, **27** disproportionates rapidly into *S*-methyl methanethiosulfonate (**28**) and dimethyl disulfide (**29**).

[13]) The results obtained in the perilla model system described below suggest that an internal base, such as an alkoxide anion situated on the C_3-side chain, is required for that elimination.

[14]) The isolated product was optically inactive and seemed to be homogeneous as judged by capillary GLC and ^{1}H-NMR spectroscopy (400 MHz), but the fact that four signals (149.5, 42.6, 42.4, and 35.8 ppm) in its ^{13}C-NMR spectrum were doubled, indicated that the major product was in fact a 1:1 mixture of diastereoisomers.

Scheme 10



discussed before, no elimination product corresponding to **15** could be detected[15]). We consider this as a hint that the observed elimination in the former series (see *Scheme 8*) is triggered by an internal alkoxide base[13]). Furthermore, we were unable to detect any thiosulfonic esters, the expected disproportion companions of **40** and **41**/**41'** corresponding to **28** (see *Scheme 8*). Therefore, it seems as if an other, as yet unidentified component of the reaction mixture reduces the intermediate thiosulfinates to the corresponding disulfides.

---

[15]) The crude reaction mixture did not discolor a solution of 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione. This result provides clear-cut evidence that no 1,3-dienes that can assume a s-*cis* conformation were present in this mixture.

5. Conclusion. – The unprecedented reactivity of γ,δ-epoxy-ketones towards the dimsyl anion obviously calls for further studies. We are presently evaluating the synthetic potential of some of the reactions that were discovered in the course of the investigations discussed in the present paper.

The authors would like to thank the Eidgenössische Technische Hochschule, Zürich, for a research grant (project 0-20-293-89).

Experimental Part

1. *General.* See [20]. GC-MS: *HP 5890* series *II* GC with *HP 5971A* MS, EI (70 eV), T = 190°; columns: 30 m, ∅ 0.25 mm, film thickness 0.25 μm; column *1*, *SPB 5* (*Supelco*); column *2*, *DB 210* (*J & W*); column *3*, *Supelcowax 10* (*Supelco*); flow, 0.3 ms^{-1} He; program *A*: column *1*, 50–120° (70°/min), 120–180° (4°/min), and 180–240° (20°/min, hold 7 min); program *B*: column *1*, 50–120° (70°/min), 120–140° (1°/min), and 140–240° (20°/min, hold 7 min); program *C*: column *2*, 50–90° (70°/min) and 90–240° (10°/min, hold 20 min); program *D*: column *2*, 50–180 (50°/min); program *E*: column *3*, temp. as in *B*.

2. *(1RS,2RS,1'SR)-1-(4',4'-Dimethyl-2',3'-dimethylidenecyclohexyl)propane-1,2-diol* (**15**). To a soln. of 3.08 g (27.44 mmol) of *t*-BuOK (*Fluka, puriss.*; freshly sublimed) in 50 ml of DMSO (*Fluka, puriss.*; stored over molecular sieves) was added 1.00 g (5.48 mmol) of **7** [1] at 25° under Ar. After stirring at r.t. for 10 h, the mixture was poured on crushed ice and worked up with Et_2O. The resulting yellow oil (0.89 g) was chromatographed (hexane/AcOEt 2:1) to give (in the order of elution) 100 mg (10%) of **12**, 263 mg (23%) of **15**, 12 mg (0.7%) of **16**, and 132 mg (12%) of **13**/**14** 4:1.

Data of **15**: M.p. 105° (Et_2O/hexane). UV (EtOH): 215 (3.77). IR ($CHCl_3$): 3570, 3440, 3090, 2970, 2935, 2870, 1629, 1621, 1456, 1380, 1117, 1049, 978, 902, 846, 827. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.97 (*d*, *J* = 2.4, 1 H); 4.82 (*dd*, *J* = 2.4, 0.8, 1 H); 4.78 (*d*, *J* = 1.9, 1 H); 4.70 (*d*, *J* = 1.9, 1 H); 3.88 (*qd*, *J* = 6.4, 2.7, 1 H); 3.41 (*dd*, *J* = 8.6, 2.7, 1 H); 2.47 (*dt*, *J* = 8.6, 4.5, 1 H); 1.97 (*dq*, *J* = 13.5, 4.5, 1 H); 1.9–1.5 (br., exchangeable with D_2O, 2 H); 1.78 (*dddd*, *J* = 13.5, 11.5, 5.0, 4.0, 1 H); 1.63 (*dd*, *J* = 13.5, 12.4, 1 H); 1.36 (*dt*, *J* = 13.2, 4.5, 1 H); 1.20 (*d*, *J* = 6.4, 3 H); 1.10 (*s*, 3 H); 1.02 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 158.0 (*s*); 151.0 (*s*); 111.4 (*t*); 106.9 (*t*); 73.5 (*d*); 66.7 (*d*); 46.6 (*d*); 37.3 (*s*); 36.4 (*t*); 28.1 (*q*); 27.6 (*q*); 22.7 (*t*); 20.5 (*q*). MS: 210 (1, M^+), 195 (3), 177 (5), 165 (3), 137 (78), 136 (64), 121 (100), 107 (23), 105 (10), 95 (14), 93 (31), 91 (12), 81 (12), 79 (12), 75 (14), 74 (19), 57 (21), 45 (14), 41 (15). Anal. calc. for $C_{13}H_{22}O_2$ (210.32): C 74.24, H 10.54; found: C 74.41, H 10.45.

Data of (1RS,2RS,1'SR,2'RS)-1-[4',4'-Dimethyl-2'-(methyldithiomethyl)-3'-methylidenecyclohexyl]propane-1,2-diol (**16**): Oil. IR ($CHCl_3$): 3580, 3005, 2960, 2925, 2850, 1632, 1452, 1380, 1261, 1093, 1068, 799. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.92 (*d*, *J* = 0.9, 1 H); 4.80 (*d*, *J* = 1.5, 1 H); 3.81 (*dq*, *J* = 7.4, 6.3, 1 H); 3.55 (*dd*, *J* = 7.4, 3.2, 1 H); 3.17 (*dd*, *J* = 13.1, 4.6, 1 H); 3.09 (*dd*, *J* = 13.1, 6.6, 1 H); 2.81 (*ddm*, *J* = 6.6, 4.6, 1 H); 2.5–1.5 (br., exchangeable with D_2O, 2 H); 2.45 (*s*, 3 H); 1.80 (*tdd*, *J* = 13.2, 10.6, 4.1, 1 H); 1.55 (*dt*, *J* = 12.9, 4.2, 1 H); 1.52 (*m*, 1 H); 1.46 (*dq*, *J* = 13.2, 4.3, 1 H); 1.25 (*td*, *J* = 12.5, 4.0, 1 H); 1.16 (*d*, *J* = 6.3, 3 H); 1.11 (*s*, 3 H); 1.09 (*s*, 3 H). ^{1}H-NMR (400 MHz, C_6D_6): 4.98 (*d*, *J* = 1.5, 1 H); 4.96 (*d*, *J* = 1.0, 1 H); 3.51 (*dq*, *J* = 7.6, 5.9, 1 H); 3.47 (*dd*, *J* = 7.6, 3.0, 1 H); 3.24 (*dd*, *J* = 12.8, 3.8, 1 H); 3.11 (*dd*, *J* = 12.8, 7.0, 1 H); 3.00 (*ddddd*, *J* = 9.9, 7.0, 3.8, 1.5, 1.0, 1 H); 2.16 (*s*, 3 H); 1.81 (*dddd*, *J* = 13.3, 12.8, 11.2, 4.0, 1 H); 1.46 (*dddd*, *J* = 11.0, 9.9, 4, 3, 1 H); 1.4–1.1 (br., 2 H); 1.40 (*dt*, *J* = 13.1, 4.2, 1 H); 1.22 (*dq*, *J* = 13.6, 4.1, 1 H); 1.12 (*td*, *J* = 12.9, 4.3, 1 H); 1.05 (*s*, 6 H); 0.91 (*d*, *J* = 5.9, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 156.6 (*s*); 106.3 (*t*); 75.8 (*d*); 69.0 (*d*); 43.4 (*d*); 41.24 (*d*); 41.19 (*t*); 39.7 (*t*); 36.7 (*s*); 29.7 (*q*); 26.8 (*q*); 23.1 (*q*); 20.0 (*t*); 19.1 (*q*). GC-MS (program *A*): t_R 23.09 min; 290 (11, M^+), 245 (4), 244 (13), 243 (70), 225 (31), 207 (14), 181 (25), 169 (39), 167 (100), 151 (14), 137 (60), 135 (76), 133 (21), 123 (32), 121 (42), 119 (32), 109 (29), 107 (67), 105 (34), 95 (73), 93 (93), 81 (69), 79 (57), 67 (40), 57 (72), 55 (32), 53 (16), 43 (31), 41 (35).

Data of (5RS,1'SR)-5-(1'-Hydroxyprop-2-enyl)-2,2-dimethylcyclohexanone (**12**): Oil. IR ($CHCl_3$): 3610, 3005, 2970, 2930, 2865, 1699, 1469, 1451, 1426, 1385, 1364, 1148, 1100, 1032, 1008, 991, 931. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.86 (*ddd*, *J* = 17.1, 10.5, 6.4, 1 H); 5.25 (*dt*, *J* = 17.1, 1.4, 1 H); 5.21 (*dt*, *J* = 10.5, 1.3, 1 H); 4.04 (*m*, 1 H); 2.44 (*dd*, *J* = 14.2, 12.2, 1 H); 2.36 (*ddd*, *J* = 14.2, 4.7, 1.7, 1 H); 1.89 (*dtt*, *J* = 12.1, 9.9, 4.8, 1 H); 1.79 (*m*, 1 H); 1.72 (*m*, 2 H); 1.58 (br. *s*, 1 H); 1.57 (*m*, 1 H); 1.15 (*s*, 3 H); 1.06 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 215.9 (*s*); 138.7 (*d*); 116.3 (*t*); 76.1 (*d*); 44.74 (*d*); 44.72 (*s*); 39.4 (*t*); 39.1 (*t*); 25.1 (*q*); 25.0 (*q*); 23.9 (*t*). GC-MS (program *E*): t_R 26.66 min; 182 (2, M^+), 167 (5), 126 (24), 125 (17), 111 (14), 97 (66), 69 (20), 57 (17), 56 (16), 55 (100), 43 (19), 39 (27).

3. *Crossover Experiment in DMSO/[$^{13}C_2$]DMSO as Solvent.* To 0.2 ml of a 1.18:1 mixture of DMSO (*Fluka puriss.*; stored over molecular sieves) and [$^{13}C_2$]DMSO [9] (containing $\geqslant$ 99% $^{13}C_2$) were added 90 mg (800 µmol) of *t*-BuOK and 15.5 mg (85 µmol) of **7**. After stirring at r.t. under Ar for 13 h, the mixture was diluted with 1.5 ml of aq. 1N HCl and worked up with Et_2O. The crude material was chromatographed as above, and the fractions obtained were analyzed by GC-MS. In addition, the NMR spectra of the major component **15*** were recorded.

Compound **15***: ^{1}H-NMR (200 MHz, $CDCl_3$): 3–1 ppm section superimposable with the one of unlabelled **15** (see above); the signals at 4.97, 4.82, 4.78, and 4.70 ppm had roughly half of the original intensity, the other half being split up through $J(^{13}C,^1H)$ of 156 Hz. ^{13}C-NMR (50 MHz, $CDCl_3$, ^{1}H-broad-band decoupled): with the chosen acquisition parameters, only two signals were clearly discernible: 111.6 (*d*, $^3J(^{13}C,^{13}C) = 3.4$); 107.2 (*d*, $^3J(^{13}C,^{13}C) = 3.4$). GC-MS (program *B*): t_R 17.66 min. MS: 197 (2.1), 195 (2.4), 179 (4.4), 178 (2.2), 177 (5.3), 165 (2.5), 163 (2.3), 161 (3.1), 159 (2.7), 139 (32), 138 (24), 137 (40), 136 (26), 123 (69), 122 (35), 121 (100), 119 (13), 109 (18), 108 (19), 107 (36), 106 (11), 105 (25), 96 (14), 95 (31), 94 (24), 93 (48), 92 (19), 91 (29), 57 (20), 55 (18), 53 (14), 45 (25), 43 (21), 41 (28).

Compound **16***: GC-MS (program *A*): t_R 22.77 min. MS: 293 (6.2), 292 (6.7), 291 (7.2), 290 (5.8), 245 (46), 244 (14), 243 (47), 227 (20), 225 (20), 209 (12), 207 (15), 183 (18), 181 (19), 177 (10), 175 (10), 171 (24), 170 (12), 169 (79), 168 (16), 167 (68), 165 (13), 152 (11), 151 (22), 149 (23), 147 (14), 139 (33), 138 (18), 137 (77), 136 (16), 135 (57), 134 (11), 133 (21), 131 (18), 127 (12), 125 (18), 124 (19), 123 (41), 122 (23), 121 (44), 120 (14), 119 (28), 115 (11), 113 (17), 111 (23), 110 (17), 109 (41), 108 (28), 107 (63), 106 (17), 105 (31), 99 (14), 97 (31), 96 (30), 95 (81), 94 (48), 93 (75), 92 (24), 91 (46), 83 (22), 82 (27), 81 (66), 80 (37), 79 (64), 78 (21), 77 (37), 75 (25), 69 (34), 68 (20), 67 (42), 58 (14), 57 (79), 56 (17), 55 (49), 53 (26), 47 (13), 46 (20), 45 (100), 43 (57), 42 (19), 41 (62), 40 (10), 39 (25).

4. *(4*RS,*5*RS,*1'*SR*)-4-(4',4'-Dimethyl-2',3'-dimethylidenecyclohexyl)-2,2,5-trimethyl-1,3-dioxolane* (**17**). To a soln. of 80 mg (0.38 mmol) of **15** in 8 ml of benzene were added 94 µl (0.76 µmol) of acetone dimethyl acetal (*Fluka, purum*) and 10 mg of *Amberlyst 15* (*Fluka*; washed successively with 5N HCl, H_2O, MeOH, and CH_2Cl_2). The resulting suspension was stirred at r.t. for 27 h and then filtered through a little anh. K_2CO_3. The filtrate was evaporated and the residue purified by FC (hexane/Et_2O 25:1) to give 85.5 mg (90%) of **17**. Oil. IR ($CHCl_3$): 3090, 3080, 2980, 2940, 2870, 1630, 1618, 1454, 1380, 1370, 1237, 1170, 1083, 1060, 1032, 989, 933, 902, 759, 743. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.93 (*d*, *J* = 2.5, 1 H); 4.81 (*dd*, *J* = 2.5, 0.5, 1 H); 4.77 (*d*, *J* = 1.8, 1 H); 4.75 (*d*, *J* = 1.8, 1 H); 3.86 (*dq*, *J* = 7.4, 6.0, 1 H); 3.62 (*dd*, *J* = 9.3, 7.4, 1 H); 2.39 (*dt*, *J* = 9.4, 4.0, 1 H); 2.01 (*dq*, *J* = 13.1, 4.0, 1 H); 1.81 (*tt*, *J* = 12.8, 4.4, 1 H); 1.64 (*td*, *J* = 13.0, 3.7, 1 H); 1.39 (*d*, *J* = 0.4, 3 H); 1.37 (*d*, *J* = 0.4, 3 H); 1.34 (*dt*, *J* = 13.5, 4.3, 1 H); 1.20 (*d*, *J* = 6.0, 3 H); 1.13 (*s*, 3 H); 1.01 (*s*, 3 H). NOE: irrad. at 3.86→5 signals at 4.81, 3.62, 2.39, 1.37, and 1.20; irrad. at 3.62→6 signals at 4.81, 3.86, 2.39, 1.64, 1.39, and 1.20. ^{13}C-NMR (75 MHz, $CDCl_3$): 157.4 (*s*); 149.3 (*s*); 111.8 (*t*); 107.5 (*t*); 107.3 (*s*); 79.8 (*d*); 76.8 (*d*); 48.1 (*d*); 37.2 (*s*); 35.5 (*t*); 28.3 (*q*); 27.5 (*q*); 27.4 (*q*); 27.3 (*q*); 23.8 (*t*); 19.6 (*q*). MS: 250 (10, M^+), 235 (43), 207 (28), 193 (28), 192 (26), 177 (30), 175 (48), 136 (31), 135 (36), 133 (35), 121 (42), 119 (52), 116 (52), 115 (100), 114 (62), 107 (36), 105 (53), 97 (60), 93 (43), 91 (59), 86 (45), 79 (42), 77 (47), 59 (79), 58 (47), 57 (68), 55 (66), 45 (48), 43 (97), 41 (59), 39 (37).

5. *(1*RS,*6*SR,*8*RS,*9*RS*)-4,4,8-Trimethyl-5-methylidene-6-[(phenylseleno)methyl]-7-oxabicyclo[4.3.0]non-9-yl Acetate* (**18**). To a soln. of 20 mg (95 µmol) of **15** and 8.5 µl (105 µmol) of pyridine in 1 ml of CH_2Cl_2 were added 20.1 mg (105 µmol) of PhSeCl (*Fluka, pract.*) at −70°. After stirring for 1 h at −70°, the solvent was evaporated and the residue purified by FC (hexane/AcOEt 2:1) to give 20.6 mg (59%) of an alcohol. To a soln. of this product in 0.5 ml of benzene were added 8.6 mg (85 µmol) of Et_3N, 8.6 mg (85 µmol) of Ac_2O and 2.5 mg (15 µmol) of 4-(pyrrolidin-1-yl)pyridine (*Fluka, puriss.*). The resulting soln. was stirred at r.t. for 16 h, then the solvent removed, and the product purified by FC (hexane/Et_2O 9:1): 15 mg (65%) of **18**. Oil. IR ($CHCl_3$): 3080, 3060, 2965, 2935, 2865, 1732, 1580, 1479, 1458, 1438, 1388, 1376, 1251, 1055, 1022, 922, 690. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.54 (*dm*, *J* = 8.0, 2 H); 7.00 (*m*, 3 H); 5.49 (*d*, *J* = 1.1, 1 H); 5.12 (*d*, *J* = 0.8, 1 H); 4.97 (*t*, *J* = 5.6, 1 H); 4.04 (*quint.*, *J* = 6.1, 1 H); 3.40 (*d*, *J* = 12.0, 1 H); 3.26 (*d*, *J* = 12.0, 1 H); 2.68 (*q*, *J* = 5.7, 1 H); 2.14 (*s*, 3 H); 1.86 (*m*, 1 H); 1.49 (*m*, 2 H); 1.31 (*m*, 1 H); 1.16 (*s*, 3 H); 1.14 (*d*, *J* = 6.4, 3 H); 1.08 (*s*, 3 H). NOE: irrad. at 5.49→4 signals at 5.12, 4.04, 3.40, and 3.26; irrad. at 5.12→2 signals at 5.49 and 1.16; irrad. at 4.97→6 signals at 4.04, 3.40, 3.26, 2.68, 2.14, and 1.49. ^{13}C-NMR (100 MHz, $CDCl_3$): 171.0 (*s*); 155.0 (*s*); 132.7 (2*d*); 131.7 (*s*); 128.9 (2*d*); 126.6 (*d*); 110.9 (*t*); 83.5 (*s*); 79.3 (*d*); 72.7 (*d*); 49.7 (*d*); 41.1 (*t*); 35.6 (*t*); 35.5 (*s*); 30.9 (*q*); 30.1 (*q*); 21.1 (*t*); 21.0 (*q*); 14.6 (*q*). MS: 410 (1.4), 409 (1.7), 408 (6.4), 407 (1.1), 406 (3.4), 405 (1.5), 404 (1.3), 348 (1), 237 (1), 191 (35), 178 (32), 177 (100), 159 (24), 135 (10), 93 (12), 77 (12), 43 (42).

6. *Separation of* **13**/**14** *by Treatment with 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione: 5,8-Dihydro-5,11,11-trimethyl-2-phenyl-7-(2,2,5-trimethyl-1,3-dioxolan-4-yl)-5,8-ethano-1*H*-[1,2,4]triazolo[1,2-a]pyridazine-1,3-(2*H*)-dione* (**19**/**20**). To a soln. of 30.9 mg (0.079 mmol) of 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)dione (*Fluka, purum*) in 1 ml of acetone were added 65 mg (0.331 mmol) of **13**/**14** 4:1 (see above). After stirring at r.t. for 5 min,

the solvent was evaporated and the residue chromatographed (hexane/AcOEt 1:1) to give 13.5 mg (21%) of **13** as a very unstable oil and 12.4 mg (10%) of a mixture of diastereoisomeric *Diels-Alder* adducts. This mixture was dissolved in 1 ml of benzene and treated with 9.2 µl (75 µmol) of acetone dimethyl acetal (*Fluka, purum*) and 5 mg of *Amberlyst 15* (*Fluka*; washed as described above). After stirring for 3 h at r.t., the solvent was evaporated and the residue chromatographed to give 7 mg of the major isomer (**19** or **20**) and 2.1 mg of the minor isomer (**20** or **19**).

*Data of (1*RS,*2*RS*)-1-(4',4'-Dimethyl-3'-methylidenecyclohex-1-enyl)propane-1,2-diol* (**13**): ^{1}H-NMR (200 MHz, $CDCl_3$): 6.12 (*s*, 1 H); 4.98 (*s*, 1 H); 4.83 (*s*, 1 H); 3.83 (*m*, 1 H); 3.80 (*m*, 1 H); 2.4 (br. *s*, exchangeable with D_2O, 2 H); 2.28 (*dtd*, *J* = 18.0, 5.5, 1.0, 1 H); 2.00 (*dtd*, *J* = 18.0, 7.0, 1.5, 1 H); 1.49 (*m*, 2 H); 1.14 (*d*, *J* = 6.0, 3 H); 1.09 (*s*, 3 H); 1.04 (*s*, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 152.0 (*s*); 128.4 (*t*); 113.3 (*s*); 110.4 (*d*); 81.2 (*d*); 69.5 (*d*); 36.7 (*t*); 34.0 (*s*); 28.0 (*q*); 27.8 (*q*); 22.3 (*t*); 19.1 (*q*). GC-MS (program *A*): t_R 12.32 min; 196 (2, M^+), 152 (26), 151 (100), 137 (25), 95 (11), 91 (13), 67 (15).

Data of the Major Adduct (**19** or **20**): IR ($CHCl_3$): 3010, 2980, 2940, 2870, 1757, 1712, 1704, 1502, 1457, 1448, 1409, 1382, 1373, 1269, 1237, 1172, 1148, 1105, 1091, 1035, 860. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.5–7.3 (*m*, 5 H); 6.16 (*d*, *J* = 1.7, 1 H); 4.96 (*ddd*, *J* = 3.4, 2.4, 1.7, 1 H); 4.00 (*dq*, *J* = 8.8, 5.6, 1 H); 3.94 (*d*, *J* = 8.8, 1 H); 2.06 (*dd*, *J* = 13.0, 3.4, 1 H); 1.89 (*s*, 3 H); 1.52 (*dd*, *J* = 13.0, 2.4, 1 H); 1.47 (*s*, 3 H); 1.44 (*s*, 3 H); 1.28 (*s*, 3 H); 1.16 (*d*, *J* = 5.6, 3 H); 0.97 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 154.1 (*s*); 138.6 (*s*); 132.6 (*d*); 131.4 (*s*); 129.1 (2*d*); 128.2 (2*d*); 125.6 (*d*); 109.0 (*s*); 81.9 (*d*); 74.2 (*d*); 66.6 (*s*); 50.0 (*d*); 41.0 (*t*); 36.9 (*s*); 27.4 (2*q*); 26.8 (*q*); 25.5 (*q*); 15.9 (*q*); 15.6 (*q*); one *s* missing. MS: 411 (1, M^+), 396 (5), 356 (40), 355 (100), 218 (11), 164 (24), 135 (10), 119 (18), 107 (12), 91 (17), 86 (33), 58 (21), 43 (33).

Data of the Minor Adduct (**20** or **19**): IR ($CHCl_3$): 2975, 2935, 2870, 1758, 1709, 1503, 1409, 1382, 1262, 1173, 1096, 1043, 854, 688. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.5–7.2 (*m*, 5 H); 6.15 (*t*, *J* = 1.3, 1 H); 4.82 (*dt*, *J* = 3.3, 2.1, 1 H); 3.98 (*dd*, *J* = 8.5, 1.1, 1 H); 3.77 (*dq*, *J* = 8.5, 6.0, 1 H); 2.00 (*dd*, *J* = 13.0, 3.5, 1 H); 1.83 (*s*, 3 H); 1.48 (*s*, 3 H); 1.37 (*s*, 3 H); 1.33 (*m*, 1 H); 1.29 (*d*, *J* = 6.0, 3 H); 1.20 (*s*, 3 H); 0.87 (*s*, 3 H). MS: 411 (1, M^+), 396 (5), 356 (33), 355 (100), 164 (21), 135 (10), 119 (18), 107 (12), 91 (17), 86 (30), 58 (19), 43 (34).

7. *(*S*)-7-(Methylthio)*-p-*mentha-1,8-diene* (**31**). To a soln. of 2.0 g (13.14 mmol) of (*S*)-perilla alcohol (**30**; *Aldrich*) in 30 ml of pyridine were added 3.5 ml (39.4 mmol) of dimethyl disulfide (*Fluka, pract.*) and 9.7 ml (39.4 mmol) of tributylphosphine (*Fluka, techn.*). The mixture was stirred at r.t. for 6 days and then worked up with Et_2O/10% aq. HCl soln. The crude product was purified by FC (hexane) and bulb-to-bulb distillation (220°/100 mbar): 1.58 g (66%) of **31**. IR ($CHCl_3$): 3080, 2960, 2910, 2855, 2835, 1643, 1451, 1433, 1372, 1232, 913, 889. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.56 (*m*, 1 H); 4.73 (*m*, 1 H); 4.71 (*m*, 1 H); 3.05 (*d*, *J* = 14.2, 1 H); 3.03 (*d*, *J* = 14.2, 1 H); 2.15 (*m*, 4 H); 1.97 (*s*, 3 H); 1.96 (*m*, 1 H); 1.85 (*m*, 1 H); 1.74 (*s*, 3 H); 1.49 (*dddd*, *J* = 12.7, 11.4, 10.3, 6.4, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 149.8 (*s*); 133.1 (*s*); 124.4 (*d*); 108.7 (*t*); 41.2 (*t*); 41.0 (*d*); 30.7 (*t*); 27.7 (*t*); 27.2 (*t*); 20.8 (*q*); 14.5 (*q*). GC-MS (program *D*): t_R 6.42 min; 184 (3.9), 183 (9.4), 182 (77, M^+), 135 (21), 134 (46), 121 (15), 119 (57), 107 (26), 106 (21), 105 (33), 99 (39), 93 (83), 92 (42), 91 (100), 79 (71), 77 (54), 68 (31), 67 (35), 65 (30), 53 (27), 41 (49), 39 (48).

8. *(4*S*)-7-(Methylsulfinyl)*-p-*mentha-1,8-diene* (**32**/**33**). To a soln. of 586 mg (2.74 mmol) of $NaIO_4$ (*Fluka, purum*) in 80 ml of H_2O/MeOH 1:1 was added a soln. of 500 mg (2.74 mmol) of **31** in 40 ml of THF at 0°. After stirring for 4 h at 0° and 20 h at r.t., the mixture was filtered and the filtrate evaporated. The remaining aq. phase was extracted with CH_2Cl_2 (3 × 100 ml), the combined extract dried ($MgSO_4$) and evaporated, and the crude product purified by FC (AcOMe): 248 mg (56%) of **32**/**33** 1:1 (^{13}C-NMR). IR ($CHCl_3$): 3080, 2990, 2920, 2835, 1642, 1451, 1433, 1422, 1406, 1375, 1298, 1240, 1033, 981, 954, 933, 892, 660. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.80 (*m*, 1 H); 4.74 (*m*, 1 H); 4.71 (*m*, 1 H); 3.45 (*d*, *J* = 12.5, 1 H); 3.30 (*d*, *J* = 12.5, 1 H); 2.55 (*s*, 3 H); 2.3–1.95 (*m*, 5 H); 1.85 (*m*, 1 H); 1.73 (*s*, 3 H); 1.53 (*m*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 149.1 (*s*, only 1 signal for both diastereoisomers); 129.462, 129.455 (2*d*); 128.12, 128.07 (2*s*); 109.0, 108.9 (2*t*); 63.7, 63.6 (2*t*); 40.5, 40.2 (2*d*); 38.2, 38.1 (2*q*); 30.81, 30.79 (2*t*); 29.6, 29.4 (2*t*); 27.39, 27.36 (2*t*); 20.8, 20.7 (2*q*). MS: 199 (0.8), 198 (0.2, M^+), 182 (2), 135 (76), 134 (12), 119 (14), 107 (49), 105 (18), 94 (10), 93 (100), 92 (12), 91 (56), 81 (24), 79 (68), 77 (35), 67 (29), 65 (13), 55 (28), 53 (13), 41 (23), 39 (14).

9. *Treatment of* **32**/**33** *with* t-*BuOK in DMSO*. To a soln. of 300 mg (2.67 mmol) of *t*-BuOK in 3 ml of DMSO were added 87 mg (0.438 mmol) of **32**/**33** 1:1 under Ar at r.t. After stirring for 2 h, the mixture was worked up with 1N aq. HCl and Et_2O. The crude material was separated (FC, pentane) to give 21.5 mg (27%) of **40**/(±)-**41** 1:1 and 6.9 mg (6.4%) of (±)-**39**.

Data of Bis[(5-isopropenyl-2-methylidenecyclohexyl)methyl] Disulfide (**40**/(±)-**41**): $[\alpha]_D = 0 \pm 0.5$ (*c* = 1.0, CCl_4). IR (CCl_4): 3070, 2955, 2925, 2850, 1643, 1461, 1454, 1377, 906. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.74 (*m*, 4 H); 4.72 (*m*, 2 H); 4.70 (*m*, 2 H); 2.92 (*ddd*, *J* = 12.9, 7.9, 2.7, 2 H); 2.86 (*dd*, *J* = 12.8, 7.6, 2 H); 2.74 (*m*, 2 H); 2.24 (*dt*, *J* = 13.7, 4, 2 H); 2.17 (*m*, 4 H); 1.95 (*ddt*, *J* = 13.2, 5.4, 3.9, 2 H); 1.83 (*dm*, *J* = 13, 2 H); 1.72 (*s*, 6 H); 1.56 (*tdd*,

J = 13.2, 5.0, 3.0, 2 H); 1.31 (*qdd*, J = 12.8, 4.4, 1, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 149.7 (2*s*); 149.54, 149.49 (2*s*); 110.0 (2*t*); 109.3 (2*t*); 42.64, 42.56 (2*t*); 42.47, 42.39 (2*t*); 39.4 (2*d*); 35.85, 35.73 (2*t*); 33.1 (2*t*); 31.4 (2*t*); 21.1 (2*q*). GC-MS (program *D*): t_R 14.94 min; 364 (0.8), 363 (2.1), 362 (8.1, M^+), 214 (2.1), 213 (1.8), 182 (8), 181 (58), 180 (15), 149 (36), 147 (13), 137 (11), 133 (13), 121 (22), 119 (18), 107 (80), 105 (38), 97 (14), 95 (11), 93 (100), 91 (65), 81 (39), 79 (70), 77 (44), 69 (15), 67 (32), 65 (16), 55 (37), 53 (24), 41 (50), 39 (17).

*Data of (1*RS,*5*SR*)-[(5-Isopropenyl-2-methylidenecyclohexyl)methyl] Methyl Disulfide* ((±)-**39**): $[\alpha]_D$ = +5 (c = 0.25, CCl_4). IR (CCl_4): 3075, 2970, 2935, 2860, 1644, 1442, 1413, 1374, 1308, 1253, 1212, 950, 905, 896, 652. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.78 (*d*, J = 2.3, 1 H); 4.77 (*d*, J = 2.3, 1 H); 4.72 (*m*, 1 H); 4.71 (*m*, 1 H); 2.94 (*dd*, J = 12.9, 8.0, 1 H); 2.89 (*dd*, J = 12.9, 7.5, 1 H); 2.74 (*tdd*, J = 7.6, 5.1, 2.4, 1 H); 2.41 (*s*, 3 H); 2.55 (*ddd*, J = 13.7, 4.8, 3.3, 1 H); 2.21–2.10 (*m*, 2 H); 1.94 (*ddt*, J = 13.4, 3.3, 2.4, 1 H); 1.84 (*dm*, J = 12.8, 1 H); 1.72 (*m*, 3 H); 1.57 (*ddd*, J = 13.2, 12.5, 5.1, 1 H); 1.32 (*qd*, J = 12.8, 4.8, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 149.4 (*s*); 149.1 (*s*); 109.6 (*t*); 109.0 (*t*); 42.3 (*d*); 41.6 (*t*); 39.2 (*d*); 35.6 (*t*); 32.9 (*t*); 31.2 (*t*); 23.0 (*q*); 20.9 (*q*). GC-MS (program *D*): t_R 4.86 min; 230 (0.5), 229 (0.7), 228 (5.5, M^+), 181 (48), 149 (36), 121 (13), 107 (58), 105 (22), 95 (13), 93 (100), 91 (54), 81 (48), 79 (79), 77 (40), 69 (23), 67 (35), 65 (18), 55 (39), 53 (30), 47 (10), 45 (27), 43 (11), 41 (69), 39 (43), 29 (15), 27 (19).

REFERENCES

[1] E.J. Brunner, Thesis, ETH Zürich No. 8204, 1987.

[2] a) Y. Gaoni, *Tetrahedron* **1972,** *28,* 5525; b) Y. Gaoni, *ibid.* **1972,** *28,* 5533; c) F.E. Ziegler, G.R. Reid, W.L. Studt, P.A. Wender, *J. Org. Chem.* **1977,** *42,* 1991.

[3] H.-J. Borschberg, unpublished results.

[4] S. Bank, C.A. Rowe, A. Schriesheim, L.A. Naslund, *J. Org. Chem.* **1968,** *33,* 221.

[5] A.J. Hubert, H. Reimlinger, *Synthesis* **1969,** 97.

[6] a) C. Paulmier, 'Selenium Reagents and Intermediates in Organic Synthesis', Pergamon Press, Oxford, 1986, Chapt. VIII; b) K.C. Nicolaou, *Tetrahedron* **1981,** *37,* 4097.

[7] J.E. Baldwin, *J. Chem. Soc., Chem. Commun.* **1976,** 734.

[8] D.H.R. Barton, T. Shiori, D.A. Widdowson, *J. Chem. Soc. (C)* **1976,** 631.

[9] R. Beerli, H.-J. Borschberg, *J. Labelled Comp. Radiopharm.* **1991,** *29,* 957.

[10] H.-O. Kalinowski, S. Berger, S. Braun, '^{13}C-NMR-Spektroskopie', Georg Thieme Verlag, Stuttgart, 1984, Chapt. 4.

[11] W.T. Comer, D.L. Temple, *J. Org. Chem.* **1973,** *38,* 2121.

[12] a) E.J. Corey, M. Chaykovsky, *J. Am. Chem. Soc.* **1962,** *84,* 866; b) *ibid.* **1965,** *87,* 1345; c) *J. Org. Chem.* **1963,** *28,* 254; d) C. Walling, L. Bollyky, *ibid.* **1963,** *28,* 256; e) G. Tsuchihashi, S. Iruchijima, M. Ishibashi, *Tetrahedron Lett.* **1972,** 4605.

[13] a) D.E. O'Connor, W.I. Lyness, *J. Am. Chem. Soc.* **1964,** *86,* 3840; b) K. Muzika, M. Procházka, M. Palecek, *Collect. Czech. Chem. Commun.* **1969,** *34,* 635.

[14] a) R.W. Hoffmann, *Angew. Chem.* **1979,** *91,* 625; b) D.A. Evans, G.C. Andrews, *Acc. Chem. Res.* **1974,** *7,* 147; c) R.W. Hoffmann, in 'Organic Sulfur Chemistry', Eds. R.K. Freidlina and A.E. Skorova, Pergamon Press, Oxford, 1981, p. 69–80.

[15] E. Block, in 'The Chemistry of the Sulfonium Group', Eds. C.J.M. Stirling and S. Patai, John Wiley & Sons, Chichester, 1981, Chapt. 16.

[16] D.R. Hogg, in 'The Chemistry of Sulphenic Acids and Their Derivatives', Ed. S. Patai, John Wiley & Sons, Chichester, 1990, Chapt. 9.

[17] a) H.J. Backer, H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas* **1954,** *73,* 129; b) E. Block, J. O'Connor, *J. Am. Chem. Soc.* **1974,** *96,* 3929.

[18] I. Nakagawa, T. Hata, *Tetrahedron Lett.* **1975,** 1409.

[19] a) N.J. Leonhard, C.R. Johnson, *J. Org. Chem.* **1962,** *27,* 282; b) C.R. Johnson, J.E. Keiser, *Org. Synth.* **1966,** *46,* 78.

[20] R. Beerli, H.-J. Borschberg, *Helv. Chim. Acta* **1991,** *74,* 110.