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THE MICHAEL INDUCED RAMBERG-BÄCKLUND HOMOLOGATION TO CONJUGATED ISOPRENOIDS

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Abstract Treatment of the sulfones **1** or **2** with sodium phenylsulfinate in DMSO affords the head-to-tail coupled conjugated monoterpenoids **5–8** in comparable amounts. The corresponding reaction of **3** gives the isomers **16** and **17**. The tail-to-tail homologation of **4** furnishes chiefly a 2*E*,4*E*/*Z*-mixture of the conjugated isoprenoids **18** and **19**. The various isoprenoid mixtures are separated into their components and the configuration of the isomers is established by ^{1}H NMR double resonance and the NMR:NOE technique. The head-to-tail and tail-to-tail coupled isoprenoid mixtures **5–8** and **18–21**, respectively, are isomerized to 2*E*;*Z*, 4*E*-mixtures in a 2:1 ratio. The C_{15}-sulfones **11** and **13** are obtained by treatment of **1** with the head-functionalized isoprene synthon **10**. Some speculations on the stereochemical course of the MIRB-homologation are presented

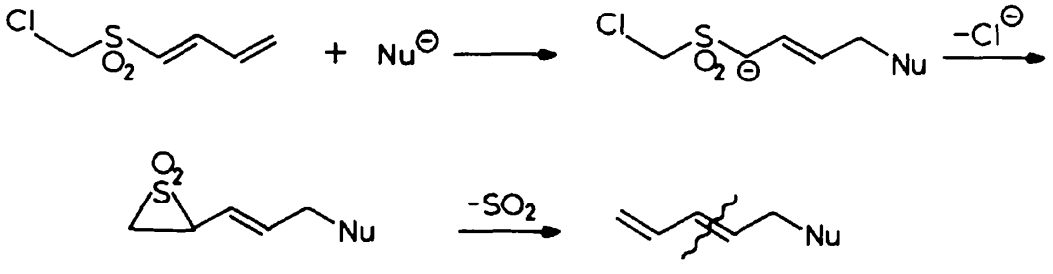
Out of the many isoprenoid homologations published in the literature only a few lead to conjugated polyenes. For a long time this group of isoprenoids was predominantly synthesized with the aid of Horner–Wittig type reactions.[1] More recently a variety of sulfur containing synthons has come to use and the unsaturation is introduced by base-catalyzed elimination of sulfinic acid.[2] Surprisingly, the Ramberg-Bäcklund reaction[3]—though excellent for the formation of olefins—has found little application in the isoprenoid field. At present only two cases have come to our knowledge, *viz* a synthesis of *β*-carotene[4] and of some unsaturated acids of isoprenoid nature.[5] During our search after improved homologation methods of functionalized isoprenes we have developed an approach to conjugated isoprenoid polyenes based on our earlier finding that chloromethyl butadienyl sulfone reacts with a suitable nucleophile to give an intermediate adduct-anion, that is trapped in a halosulfone rearrangement (MIRB-synthesis[6]: Scheme 1). The isoprene directed modification of the above mentioned MIRB-reaction allows the step by step addition of an arbitrary number of isoprene synthons in a head-to-tail or tail-to-tail fashion starting from a tail-functionalized isoprenoid halide (Scheme 2). *Z*-2-Methyl-1,3-butadienylsulfinate anion[7] serves as a 5-carbon synthon and is attached to the carbon chain with its head-functionality. The halogen is then reintroduced by successive reactions with base and hexachloroethane (HCE). The actual homologation step is effected by a nucleophile.

In earlier publications we have reported the synthesis[8] and the chlorination[9] of some unsaturated sulfones suited for the head-to-tail homologation. The sulfinate anion induced isomerization (Scheme 2), required for the tail-to-tail coupling, will be described separately.[10] In this communication we wish to report our first results on the homologation of the chlorosulfones **1–4**. As nucleophiles we have used potassium *Z*-2-methyl-1,3-butadienylsulfinate and sodium phenylsulfinate. The former can be used during the build-up of the isoprenoid skeleton, the latter may serve as a terminal synthon to be reductively split off after the required chain length has been attained.

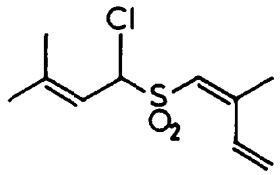
RESULTS AND DISCUSSION

Head-to-tail homologation of **1** *or* **2** *with sodium phenylsulfinate*

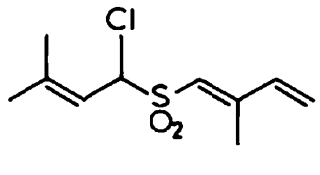
To achieve head-to-tail homologation of **1** and **2**, a variety of reaction conditions, nucleophiles and solvents have been tested. The best results were



Scheme 1.



1



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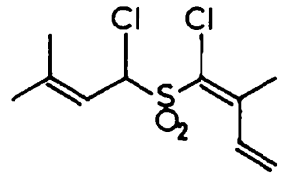

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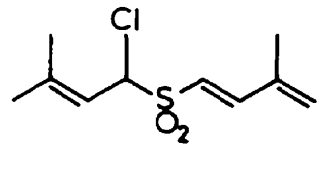

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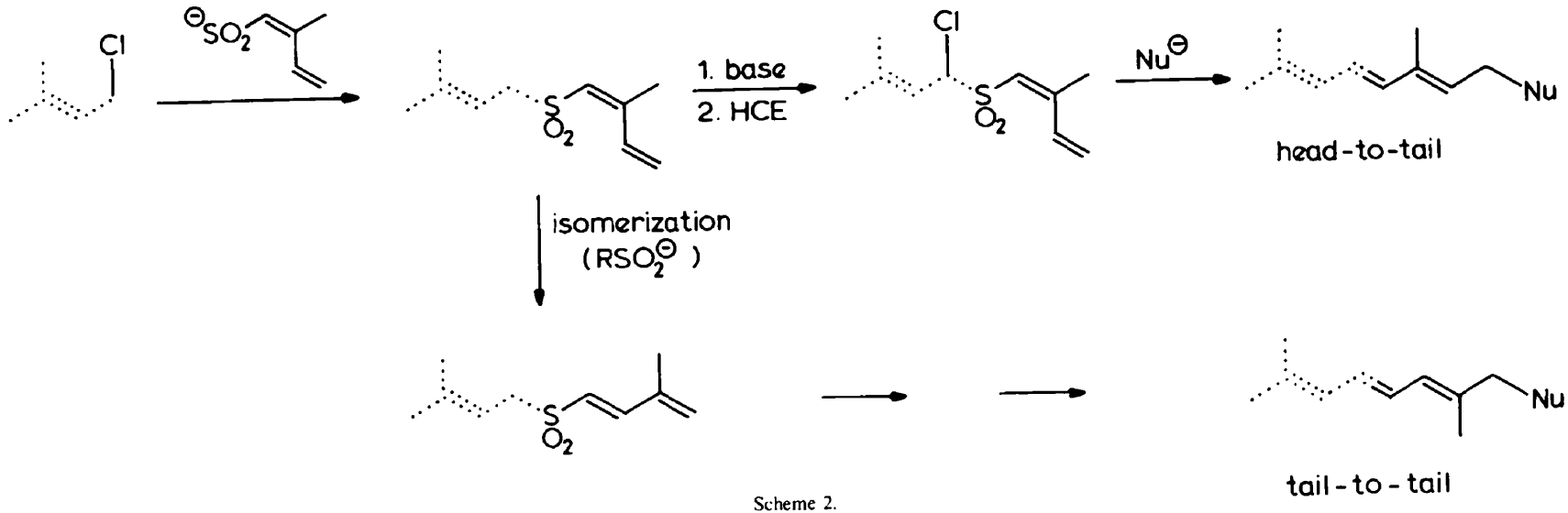


Scheme 2.

obtained with one equivalent of phenylsulfinate anion in DMSO at room temperature under exclusion of light. The use of d_6-DMSO allowed ^{1}H NMR monitoring of the reaction. The conversion of the *Z*-monochlorosulfone **1** was completed in a few minutes and a mixture of the four phenylsulfonyl substituted octatrienes **5–8** was formed (Scheme 3). The configuration of the starting chlorosulfone did not affect the product composition, since both **1** and **2** afforded identical octatriene mixtures. Prolonged manipulation of these mixtures in daylight resulted in the formation of the cyclized isomer **9**.[11] The cyclization could be suppressed by performing the chromatographic purification in dimmed light. In this way the isomer mixture was obtained free from **9** in 65–80% yield. The separation of the mixture into the components was achieved by low pressure liquid chromatography. The configurations around the C_2–C_3 double bonds of the isomers were established by NMR–NOE observations on the C_2-vinyl-signals under irradiation of the C_3-Me-absorptions. The C_4 C_5 stereochemistry followed from the J_{45} obtained by ^{1}H NMR double resonance. The ^{1}H NMR-data of the isomers **5–8** are given in Table 1. The isomer distribution in the octatriene mixture, given in Scheme 3, was calculated from several non-coinciding ^{1}H NMR-signals. Isomerization with 0.1 equivalent of iodine in $CHCl_3$ at room temperature for not longer than 2 hr in the dark gave a mixture, consisting of the all-*E*-isomer **5** and 2*Z*,4*E*-isomer **7** in a 2:1 ratio. Prolonged iodine-catalyzed or light-induced isomerization was attended with decomposition.

Head-to-tail homologation of **1** *or* **2** *using* **10**

The homologations of **1** and **2** with head-functionalized isoprene synthon **10** (Scheme 4) under the same reaction circumstances as described above, required 68 hr at room temperature. Otherwise the reaction proceeded in the same way and gave an octatriene mixture, consisting of 71% of **11**–**13**† and 29% of the 2*Z*,4*Z*-isomer **14**.

The octatrienes were obtained in 68% yield after one fast passage through a short silica-column in order to remove the cyclized sulfone **15**. From this mixture only the 2*Z*,4*Z*-isomer **14** was isolated in a pure state by low pressure liquid chromatography. Iodine-catalyzed isomerization of the original mixture furnished the 2*E*,4*E*-isomer **11** and the 2*Z*,4*E*-isomer **13** in a 2:1 ratio.‡ This mixture was separated into the components. We were unable to isolate the 2*E*,4*Z*-isomer **12**.

Head-to-tail homologation of **3** *with sodium phenylsulfinate*

Treatment of the α,α′-dichlorosulfone **3** with one equivalent of sodium phenylsulfinate in DMSO at room temperature gave a mixture, from which **16** and **17** were isolated by low pressure liquid chromatography in 56% and 17% yield, respectively (Scheme 5).

Table 1. 100 MHz ^{1}H NMR-data of **5–8**, **16** and **17** in $CDCl_3$ (TMS, $\delta = 0$).[a]

	2*E*,4*E* (**5**)	2*E*,4*Z* (**6**)[b]	2*Z*,4*E* (**7**)	2*Z*,4*Z* (**8**)	2*E*,4*Z* (**16**)	2*Z*,4*E* (**17**)
C1-H	3.93 (d)	3.93 (d)	3.96 (d)	3.76 (d)	4.02 (d)	3.95 (d)
C2-H	5.39 (t)	5.44 (t)	5.27 (t)	5.37 (t)	6.00 (t)	5.57 (t)
C3-Me	1.46 (s)	1.51 (s)	1.88 (s)	1.76 (s)	1.66 (s)	1.53 (s)
C4-H	6.09 (d)	5.63 (m)	5.97 (d)	5.16 (d)		
C5-H	6.41 (q)	6.16 (m)	6.44 (q)	6.12 (t)	6.58 (d)	6.46 (d)
C6-H[c]	5.87 (d)	6.17 (m)	5.75 (d)	5.68 (d)	6.31 (d)	5.89 (d)
C7-Me[d]	1.81 (s)	1.82 (s)	1.80 (s)	1.76 (s)	1.90 (s)	1.81 (s)
C8-H[d]	1.78 (s)	1.77 (s)	1.77 (s)	1.76 (s)	1.83 (s)	1.75 (s)
J_{12}	8	8	8	8	8	8
J_{45}	15	11	15	11.5		
J_{56}	10.5	11	10.5	11.5	10.5	11.5

[a] The phenyl-absorptions appeared as two multiplets in a 2:3 ratio from 7.4–8.0 ppm.

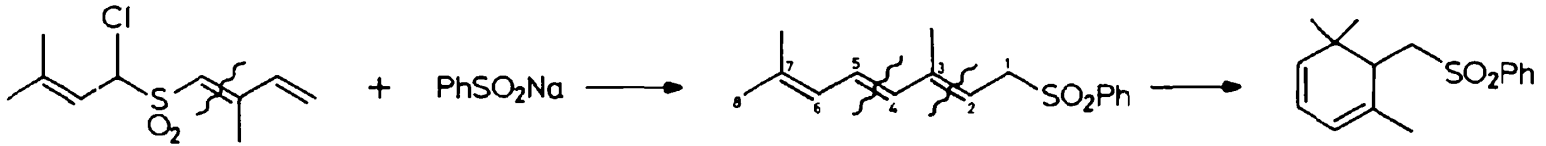
[b] The δ-values of the C4-, C5- and C6-hydrogens of compound **6** were established by spectrum simulation.

[c] All C6-H absorptions appeared as a doublet with allylic long range coupling.

[d] The C7-Me- and C8-absorptions have been arbitrarily assigned.

†Signal overlap in ^{1}H NMR did not allow the calculation of the separate percentages of **11**–**13**.

‡Traces of *E*-2-methyl-1,3-butadienyl compounds were present, seen their characteristic ^{1}H NMR signals.[8]

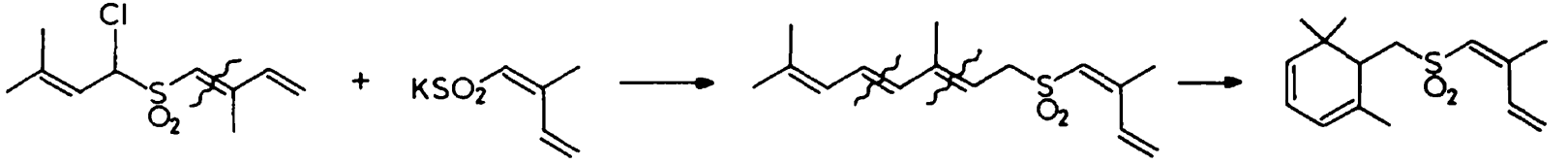


1 : *Z*
2 : *E*

5 : 2*E*, 4*E* 26%
6 : 2*E*, 4*Z* 23%
7 : 2*Z*, 4*E* 20%
8 : 2*Z*, 4*Z* 31%

9

Scheme 3.



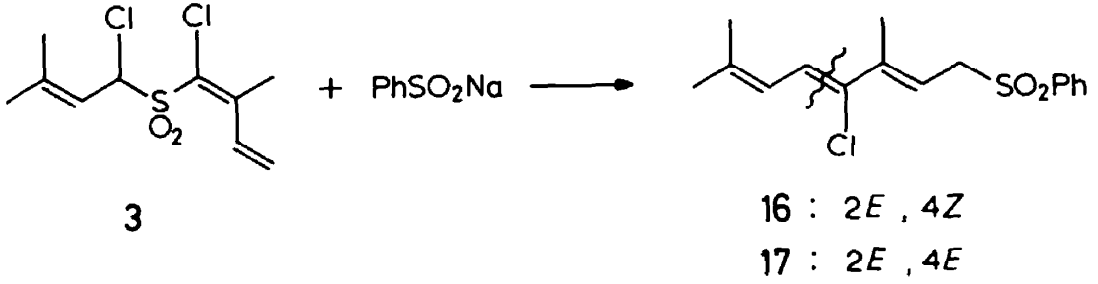
1 : *Z*
2 : *E*

10

11 : 2*E*, 4*E*
12 : 2*E*, 4*Z*
13 : 2*Z*, 4*E*
14 : 2*Z*, 4*Z*

15

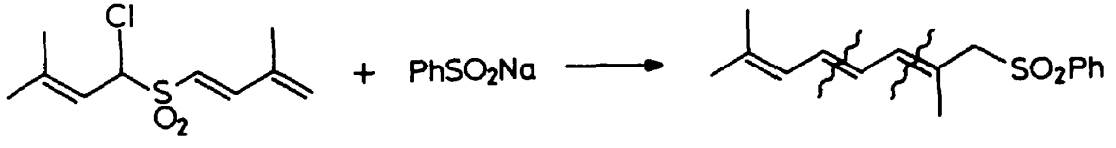
Scheme 4.



3

16 : 2E , 4Z
17 : 2E , 4E

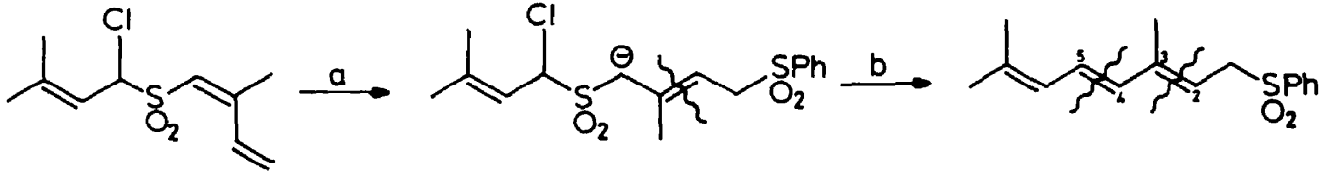
Scheme 5.



4

18 : 2E , 4E	29%
19 : 2E , 4Z	54%
20 : 2Z , 4E	7%
21 : 2Z , 4Z	10%

Scheme 6.



1 22 5-8

Scheme 7.

Table 2. 300 MHz ^{1}H NMR-data of **18–21** in $CDCl_3$ (TMS, $\delta = 0$)[a]

	2E,4E (**18**)	2E,4Z (**19**)	2Z,4E (**20**)	2Z,4Z (**21**)
C1-H	3.79 (s)	3.83 (s)	3.95 (s)	3.96 (s)
C2-Me	1.83 (d)[b]	1.86 (s)	1.90 (s)	1.97 (s)
C3-H	5.73 (d)	6.04 (d)	6.09 (d)	6.54 (d)
C4-H	6.18 (q)	5.93 (t)	5.65 (q)	5.50 (t)
C5-H	6.28 (q)	6.18 (t)	6.22 (q)	5.96 (t)
C6-H[c]	5.87 (d)	5.86 (d)	5.62 (d)	6.18 (d)
C7-Me[d]	1.80 (s)	1.79 (s)	1.77 (s)	1.83 (s)
C8-H[d]	1.74 (s)	1.74 (s)	1.71 (s)	1.73 (s)
J_{34}	10	12	11.3	11.5
J_{45}	14.7	11.5	14.5	10
J_{56}	10.5	12	11.3	11

[a] The phenyl-absorptions appeared as two multiplets in a 2 : 3 ratio from 7.4–8.0 ppm.

[b] $J = 1$ Hz.

[c] All C6-H absorptions showed allylic long range coupling.

[d] The C7-Me- and C8-absorptions have been arbitrarily assigned.

No indications were found for the presence of the two 2*Z*-isomers in the reaction mixture. The configurations of **16** and **17** were proved by the NMR-NOE technique. The ^{1}H NMR-data are taken up in Table 1.

Tail-to-tail homologation of **4** *with sodium phenylsulfinate*

The tail-to-tail homologation of **4**[10] under circumstances already described above, proceeded without formation of a cyclized sulfone, corresponding to **9** (Scheme 3). The octatrienyl sulfones **18–21** (Scheme 6) were isolated as a mixture in 80% yield after filtration through a short silica-column in order to remove traces of polymeric products. Fractions of pure isomers were obtained by low pressure liquid chromatography.

100 MHz ^{1}H NMR suffered from heavy signal overlap. For this reason the configurations of the isomers **18–21** were established by 300 MHz ^{1}H NMR (Table 2). The ratio of the isomer mixture, given in Scheme 6, was calculated from several non-coinciding ^{1}H NMR signals. It is noteworthy, that in this tail-to-tail homologation the 2*E*-content is considerably higher than in the head-to-tail homologation reported in the other sections. The iodine-catalyzed isomerization of the mixture of **18 21** in $CHCl_3$ resulted after two hours at room temperature in quantitative formation of an equilibrium-mixture, consisting of 70% of the all-*E*-isomer **18** and 30% of the 2*Z*,4*E*-isomer **20**.

Some stereochemical aspects of the MIRB homologation

The stereochemical course of the isoprenoid homologations of **1–4**, described in the preceding sections, is determined during the two successive reaction steps of the MIRB-synthesis.[6] Michael-addition of the sulfinate anion to the methylbutadienyl moiety of the starting chlorosulfone (step a) results in formation of the C_2–C_3 double bond of the octatrienes. The subsequent α-halosulfone rearrangement (Ramberg–Bäcklund reaction[3]) of the intermediate adduct-anion (step b) affords the C_4–C_5 double bond, as is illustrated for the homologation of **1** with sodium phenylsulfinate (Scheme 7).

Although the stereochemical course of the reaction is too complex to be understood without kinetical measurements, some general trends are observed. The *Z*-configuration around the C_4–C_5 double bond–determined during the Ramberg Bäcklund step–predominates in accordance with the literature.[1,2] The C_2–C_3 double bond formation (step a) is more sensitive to structural variations than step b, as can be seen from the product compositions of the octatriene mixtures (Schemes 3–6). The mixture, prepared from **1** or **2**, consists of comparable amounts of all four stereoisomers, whereas homologation of **3** and **4** leads chiefly to the two 2*E*-isomers.

When phenylsulfinic acid is used instead of its sodium salt, the Ramberg–Bäcklund step is prevented and exclusively the thermodynamically more stable *E*-adduct is formed.[13] This observation might be seen as an indication that the addition step is slower than step b with **1** or **2**, while the inverse is the case with sulfones **3** and **4**.

EXPERIMENTAL

All reactions were performed under argon in the dark. DMSO was dried over CaH_2 and distilled. Sodium

phenylsulfinate was heated for 18 hr at 150° prior to use. Chromatographic separations were carried out on pre-packed columns (Merck, Lobar, LiChroprep Si 60), using EtOAc/P.A. as an eluens at 2 atm pressure. ^{1}H NMR (TMS, $\delta = 0$, $CDCl_3$) was recorded on a Varian XL-100 and a Varian SC-300 NMR Spectrometer; IR on a Perkin–Elmer model 177 and UV on a Cary-14 spectrophotometer. M.ps were determined on a Leitz–Wetzlar apparatus and are uncorrected.

MIRB homologation of **1**–**4** *with sodium phenylsulfinate or potassium Z-2-methyl-1,3-butadienylsulfinate*

General procedure. To a DMSO soln (20 ml) of the butadienyl sulfone **1**–**4** (2 mmole) was added 1 equiv of sulfinate salt. After stirring for 30 min or 68 hr (in case of $PhSO_2Na$ or potassium Z-2-methyl-1,3-butadienylsulfinate, respectively) at r.t. the DMSO was removed *in vacuo*. Chromatographic purification of the oily residue over a silica-column (5 cm), using EtOAc/P.A. (1:5) as an eluens, afforded the isoprenoid mixtures in 65–80% yield.

Iodine catalyzed isomerization of the isoprenoid mixtures

General procedure. To a $CHCl_3$ soln (10 ml) of the isoprenoid mixture (1 mmole) at r.t. was added 25 mg (0.1 mmole) I_2. After stirring for 2–3 hr the I_2 was removed by washing with $Na_2S_2O_3$ soln. The thiosulphate-washings were extracted with $CHCl_3$. The combined $CHCl_3$-fractions were washed with water and dried over $MgSO_4$. Filtration and removal of the solvent *in vacuo* furnished quantitatively the 2*E*/*Z*,4*E*-isoprenoid mixture (*E*,*Z*-ratio 2) as an oil. The *E*,*Z*-ratio was calculated from several noncoinciding ^{1}H NMR-signals (Tables 1 and 2).

Chromatographic separation of the isoprenoid mixtures

General procedure. Repeated low pressure liquid chromatographic separations of the isoprenoid mixtures, obtained by the MIRB homologation of **1**–**4** with sulfinate salt as described in the general procedure, afforded fractions of the pure isomeric octatrienes. The compounds are described in the order of decreasing R_f-value.

Separation of **5**–**8**, *obtained from* **1** *or* **2**[8,9] *with* $PhSO_2Na$

Compound **8** (2*Z*,4*Z*-isomer) as a colourless oil. IR ($CHCl_3$): 3020, 2920, 1450 (C–H), 1645 (C=C), 1585, 1480 (phenyl), 1310, 1150, 1130 and 1090 cm^{-1} (SO_2). UV^{EtOH}_{max}: 215 (15566), 257 (12579).

Compound **6** (2*E*,4*Z*-isomer) as a colourless oil. IR ($CHCl_3$): 2930, 1450 (C–H), 1630 (C=C), 1585, 1490 (phenyl), 1320, 1310 and 1150 cm^{-1} (SO_2). UV^{EtOH}_{max}: 214 (19493), 284 (25346).

Compound **7** (2*Z*,4*E*-isomer) as a colourless oil. IR ($CHCl_3$): 2930, 1450 (C–H), 1640, 1620 (C=C), 1585, 1490 (phenyl), 1320, 1310, 1150 and 1130 cm^{-1} (SO_2). UV^{EtOH}_{max}: 285 (38846).

Compound **5** (2*E*,4*E*-isomer). M.p.: 92–94°. IR ($CHCl_3$): 3020, 2920, 1450 (C–H), 1640, 1620 (C=C), 1585, 1480 (phenyl), 1320, 1310, 1150 and 1090 cm^{-1} (SO_2). UV^{EtOH}_{max}: 217 (11862), 287 (38438). (Calc. for $C_{16}H_{20}SO_2$: C 69.53; H 7.29; S 11.60. Found: C 69.40; H 7.21; S 11.60%).

The 100 MHz ^{1}H NMR-data of **5**–**8** are given in Table 1.

Separation of **11**–**14**, *obtained from* **1** *or* **2** *with* **10**[7]

Compound **14** (2*Z*,4*Z*,1′*Z*-isomer). ^{1}H NMR ($CDCl_3$): 7.54 (C3′-H, X-part of ABX, J_{AX} 11 Hz, J_{BX} 17 Hz); 6.29 (C5-H, t, $J_{45} = J_{56}$ 11 Hz); 6.00 (C1′–H, s); 5.30–5.93 (C2′–H, C4–H, C6–H and C4′–H, m); 3.70 (C1–H, d, J_{12} 8 Hz); 2.01 (C2′–Me, d, J 1 Hz), 1.80 and 1.87 (C3–Me, C7–Me and C8–H, two s).

Compound **13** (2*Z*,4*E*,1′*Z*-isomer). ^{1}H NMR ($CDCl_3$): 7.56 (C3′–H, X-part of ABX, J_{AX} 11 Hz, J_{BX} 17 Hz); 6.60 (C5–H, q, J_{45} 15 Hz, J_{56} 10 Hz); 6.28 (C4–H, d); 6.03 (C1′–H, s), 5.90 (C6–H, d with allylic l.r.-coupling); 5.65 (C4′–H, B-part of ABX, J_{AB} 0 Hz); 5.56 (C4′–H, A-part of ABX); 5.37 (C2–H, t, J_{12} 8 Hz); 3.89 (C1–H, d); 1.97 (C2′–Me, d, J 1 Hz); 1.83 and 1.93 (C3–Me, C7–Me and C8–H, two s).

Compound **11** (2*E*,4*E*,1′*Z*-isomer). ^{1}H NMR ($CDCl_3$): 7.56 (C3′–H, X-part of ABX, J_{AX} 11 Hz, J_{BX} 17 Hz); 6.51 (C5–H, q, J_{45} 15 Hz, J_{56} 10 Hz); 6.15 (C4–H, d); 6.06 (C1′–H, s); 5.89 (C6–H, d with allylic l.r.-coupling); 5.36–5.78 (C2–H, C4′–H, m); 3.89 (C1–H, d, J_{12} 8 Hz); 2.03 (C2′–Me, d, J 1 Hz); 1.83 (C3–Me, C7–Me and C8–H, s).

The configurations of **11**, **13** and **14** are based upon comparison with the corresponding phenylsulfonyl substituted octatrienes **5**–**8**.

Separation of **16** *and* **17**, *obtained from* **3**[9,10] *with* $PhSO_2Na$

Compound **17** (2*E*,4*E*-isomer) was isolated as a colourless oil. IR ($CHCl_3$): 2940, 1460 (C–H), 1640 (C=C), 1595, 1500 (phenyl), 1330, 1320, 1165 and 1155 cm^{-1} (SO_2).

Compound **16** (2*E*,4*Z*-isomer). M.p.: 105.5–107°. IR ($CHCl_3$): 3030, 2940, 1460 (C–H), 1640, 1620 (C=C), 1330, 1320 and 1165 cm^{-1} (SO_2). (Calc. for $C_{16}H_{19}ClSO_2$: C 61.82; H 6.16; S 10.32, O 10.29, Cl 11.41. Found: C 61.76; H 6.11; S 10.42; Cl 11.45%).

The 100 MHz ^{1}H NMR-data are given in Table 1.

Separation of **18**–**21**, *obtained from* **4**[9] *with* $PhSO_2Na$

Compound **20** (2*Z*,4*E*-isomer) as a colourless oil. IR ($CHCl_3$): 3030, 2930, 1450 (C–H), 1620 (C=C), 1320, 1310 and 1150 cm^{-1} (SO_2). UV^{EtOH}_{max}: 217 (9722), 291 (33333).

Compound **21** (2*Z*,4*Z*-isomer) as a colourless oil. IR ($CHCl_3$): 3040, 2930, 1450 (C–H), 1675, 1630 (C=C), 1580, 1490 (phenyl), 1320, 1310, 1145 and 1090 cm^{-1} (SO_2). UV^{EtOH}_{max}: 218 (11452), 291 (31751).

Compound **19** (2*E*,4*Z*-isomer) as a colourless oil. IR ($CHCl_3$): 3040, 2920, 1450 (C–H), 1675, 1630 (C=C), 1585, 1485 (phenyl), 1320, 1310, 1165 and 1150 cm^{-1} (SO_2). UV^{EtOH}_{max}: 218 (10972), 292 (31555).

Compound **18** (2*E*,4*E*-isomer). M.p. 78–85°. IR ($CHCl_3$): 3040, 3020, 1450 (C–H), 1675, 1620 (C=C), 1585, 1480 (phenyl), 1320, 1310 and 1150 cm^{-1} (SO_2). UV^{EtOH}_{max}: 217 (9688), 292 (36842).

The 300 MHz ^{1}H NMR-data of **18**–**21** are given in Table 2.

Cyclization of **5**–**8** *to* **9**

Work up of the MIRB-DMSO soln (20 ml) of **5**–**8** in the light by dilution with water and extraction of the aqueous soln with $CHCl_3$ (5 × 30 ml) afforded after washing of the combined $CHCl_3$-fractions with water, drying over $MgSO_4$ and evaporation of the solvent a residue, from which the phenylsulfonyl substituted α-pyronene **9** was isolated upon column chromatography as colourless oil in variable yield. IR ($CHCl_3$): 3020, 2980, 2930, 1450 (C–H), 1645 (C=C), 1590, 1490 (phenyl), 1310, 1285, 1150, 1130, 1110 and 1085 cm^{-1} (SO_2). ^{1}H NMR ($CDCl_3$): 7.90–8.10 and 7.40–7.70 (m, phenyl), 6.43 (C4–H, m); 6.17 (C3–H, q, J_{23} 13 Hz, J_{34} 3 Hz); 5.67 (C2–H, d); 4.36 (C6–H, q, X-part of ABX, J_{AX} 10 Hz, J_{BX} 14.5 Hz); 2.97–3.36 (C7–H, m, AB-part of ABX), 2.14 (C5–Me, d, J 1 Hz); 1.22 (C1–Me, s).

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