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Some peculiarities of the preparative electroreduction of allyldimethylsulfonium salts

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The influence of electrode potential and (6-acetoxy-1-isopropenyl-4-methylhexyl)dimethylsulfonium perchlorate concentration on the yield of α-citronellyl acetate and the selectivity of reduction were studied. A mechanism of electrolytic reduction involving preparative electrolysis on a mercury cathode at potentials of the first and second waves was proposed.

Key words: electrolytic reduction; mercury cathode; allyldimethylsulfonium salts; α-citronellyl acetate.

In the previous communication[1] a new method for the synthesis of monoterpenol acetates, which can serve as intermediates in the syntheses of a series of natural products, was described. This involved electrolytic reduction (ER) of the respective readily accessible[2] allyldimethylsulfonium salts. The electrolysis conditions ensuring the selective formation of the target products[1] were selected empirically, since the literature data on the mechanism of ER of sulfonium salts are very contradictory.

It is known[3] that the two-electron ER of sulfonium salts results in the cleavage of one C—S bond in the salt to give sulfides and hydrocarbons. A mechanism involving synchronous cleavage of the C—S bond with the transfer of one electron and the elimination of the most stable radical from the intermediate in the bulk of the solution has been proposed[4,5] for the ER of arylalkylsulfonium salts on platinum and carbon-glass cathodes. However, the ER of methyldiphenylsulfonium perchlorate on a mercury cathode can follow two pathways:[6] free-radical reductive cleavage or heterolytic cleavage of the sulfonium cation adsorbed on mercury. Depending on the conditions of the ER, different ligands are eliminated, leading to changes in the ratio of the final products of the electrolysis. The most branched radicals or those possessing electron-withdrawing substituents are eliminated preferentially, which follows from an analysis of the known examples of the ER of substituted alkylsulfonium salts.[3,7] The ER of alkylsulfonium salts is complicated by the possible formation of ylides and products of their subsequent transformations.[8] For example, the products of reactions of ylides with carbonyl compounds and olefins have been isolated[9] in 7—40 % yields.

The purpose of the present work was to study the effect of various factors on the selectivity of preparative

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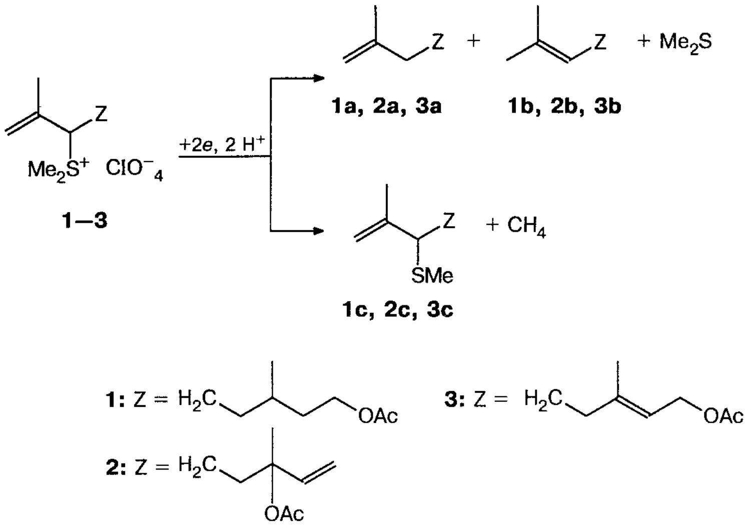
Scheme 1



ER of allyldimethylsulfonium salts and to compare the results obtained with the concepts of the mechanism of this process available in the literature.

Results and Discussion

According to the literature data,[4—7] the ER of allyldimethylsulfonium salts **1**—**3** should preferentially afford α-isoprenoids **1a**—**3a**. However, if the allyl substituent is eliminated as a kinetically independent radical species, the formation of a significant amount of the corresponding β-isomers (**1b**—**3b**) should occur. The most probable side products should involve sulfides such as RSMe (**1c**—**3c**) (Scheme 1).

According to the data of the traditional polarography and rotating disc electrode methods,[10] the ER of salts **1**—**3** is a two-step process with a first wave potential of $E^{\mathrm{I}}_{1/2} = -1.2$ V. Electrolysis of salts **1**—**3** on a mercury cathode ($E = -1.2$ V) in 90 % aqueous DMF affords α-isoprenoids **1a**—**3a** in 40—45 % yields with an insignificant admixture (5—10 %) of the β-isomers (**1b**—**3b**). The presence of the β-isomers manifests itself in the ^{1}H NMR spectra as the appearance of signals corresponding to the $Me_2C{=}CH$ moiety, *i.e.*, a broadened triplet and two singlets corresponding to the vinyl and methyl protons, respectively, at δ 5.08, 1.68, and 1.6. The ratio of the isomers in the mixture can be estimated from the ratio of the relative integral intensities of the characteristic signals of the vinyl protons in the α-isomer (broadened singlets at δ 4.64 and 4.68) and β-isomer. We did not detect sulfides **1c**—**3c** as side products of the electrolysis of salts **1**—**3**. However, we observed several rather unusual facts. The present work deals with the description and rationalization of these observations.

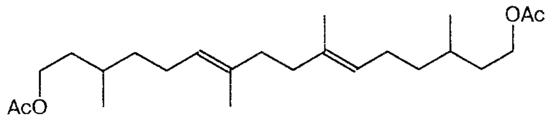
It was found that during the preparative ER of sulfonium salts **1**—**3** in dry DMF at $E = -1.1$ V, the current begins to increase abruptly after 2—3 min, which results in the disappearance of the starting salt after several minutes of electrolysis. It turned out that this "autocatalytic" increase in the current depends on the concentration of the starting sulfonium salt. To study

Table 1. Results of the preparative electrolytic reduction of (6-acetoxy-1-isopropenyl-4-methylhexyl)dimethylsulfonium perchlorate (**1**) on a mercury cathode

Run	C_1/M	E_{ER}/V	Content of H_2O in DMF (%)	Overall yield of compounds **1a** and **1b** (%)	Ratio of isomers **1a**/**1b**
1	0.1	−1.2	—	25—30	2.3
2	0.05	−1.1	—	40—45	9
3	0.05	−1.1÷−1.2	10	60—65	20
4	0.05	−1.1÷−1.7	10	75—80	20
5	0.01	−1.7	—	50	1
6	0.03	−1.7	—	40	1
7	0.025	−0.9*	—	40	1.5

Note. Background solution: 0.3 *M* $LiClO_4$. * ER in the presence of O_2.

this phenomenon in more detail, we chose salt **1** as the model compound (Table 1). The current increased fourfold in a 0.05 *M* solution of salt **1**, whereas no autocatalysis at all was observed in a 0.01 *M* solution. It should be particularly emphasized that after 2 min of ER, the current increased twofold in comparison with I_{init}; however, when we disconnected the circuit for 4 min and then connected it again, the current reached $4I_{init}$ (the same current was also observed after a pause for 10 min). These facts suggest that the starting salt undergoes a second-order reaction with a product of the electrode reaction to give species that are reduced at lower cathodic potentials than the original salt ($E \approx -0.7$ to -0.8 V), and that these species have considerable stability. The electrolysis of a 0.1 *M* solution of salt **1** (see Table 1, run *1*) under conditions of autocatalysis affords isomers **1a** and **1b** in an overall yield not exceeding 25—30 % with a significant fraction of the β-isomer. In addition, dimer **1d** is formed in a yield of about 10—15 %.



1d

The structure of dimer **1d** was established by spectroscopic methods, *viz.*, by the presence of a molecular peak and peaks corresponding to characteristic fragmentation in the mass spectrum, as well as by comparing the ^{1}H NMR spectrum of compound **1d** with that of 3,6,7,10,11,14-hexamethylhexadeca-2*E*,6*E*,10*E*,14*E*-tetraene-1,16-diol described previously.[11]

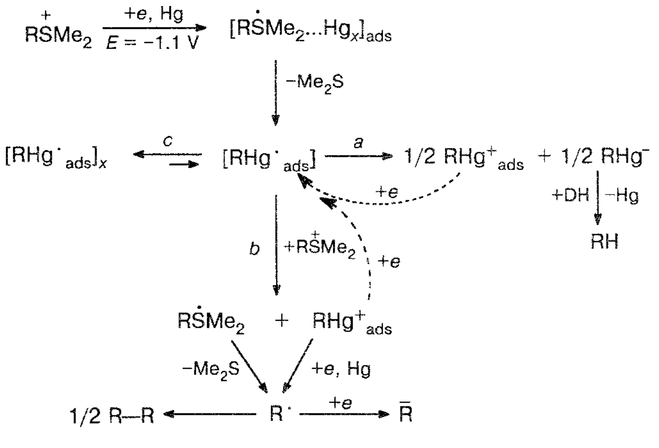
However, if the potential of the ER is shifted to $E \approx -0.6$ V during the autocatalytic current increase and then gradually shifted in the negative direction to $E = -1.1$ to -1.2 V, isoprenoids **1a** and **1b**, of which the α-isomer **1a** predominates, are formed in ~45 % yield after a charge (Q) of ~1 F mol^{-1} is passed (see Table 1, run *2*). If DMF containing 10 % H_2O is used as the solvent, the autocatalytic current increase becomes smaller. For example, in run *3* (see Table 1) the current increased only 1.5-fold with a 0.05 *M* concentration of salt **1**, and α-isoprenoid **1a** was the main product. It should be noted that only traces of dimer **1d** were found in the reaction mixtures formed in runs *2* and *3*. Obviously, the electrolysis occurs more selectively when the significant spontaneous current increase is avoided.

After $Q = 1$ F mol^{-1} has passed (at $E = -1.2$ V), polarographic monitoring indicates that the starting sulfonium salt disappears almost completely from the bulk of the solution. However, a further cathodic shift of potential (to -1.7 V) gives rise to a noticeable current. The two-step ER (first at $E \sim 1.2$ V and then at a more negative potential) causes a significant increase in the yield of the α-isoprenoid **1a** (see Table 1, run *4*); the reaction mixture contains practically no dimer **1d**.

In this case, in addition to the usual factors affecting the selectivity of the process (such as the composition of the background electrolyte, the concentration of the substrate, and the potential of electrolysis), changes in the potential during the electrolysis turns out to be the most important. These results of the electroreduction of allyldimethylsulfonium salts not only disobey the classical mechanism, but also cannot be fully explained within the scheme that we proposed previously.[10] Although disputable, Scheme 2 suggested in the present work makes it possible to explain the phenomena observed during the electrolysis of salts **1**—**3**.

It can be assumed that the transfer of one electron to a cation of the starting salt followed by elimination of Me_2S from the radical intermediate on the surface of the mercury cathode results in a stable [$RHg^{\cdot}{}_{ads}$] radical, which does not undergo reduction at $E = -1.1$ V but disproportionates (pathway *a*) into [RHg^+], *i.e.*, an organomercury cation. Obviously, this species is stable in the solution undergoing electrolysis when the polarization is switched off, while the reduction potential of this cation should be much lower than the discharge potential of the starting depolarizer. It is known[12] that EtHgBr undergoes reduction on a mercury cathode at $E = -0.4$ V, while $CH_2{=}CHCH_2HgBr$ is reduced at $E \sim -0.1$ V (*vs.* SCE; 50 % aqueous dioxane, pH = 7). However, $(CH_2{=}CHCH_2)_2Hg$ is reduced under the same conditions at a much more cathodic potential ($E < -1.0$ V).

Scheme 2



We believe that during the starting period of electrolysis, particularly at a high concentration of the starting salt (as in run *1*, see Table 1), the electron transfer occurs not only from the cathode resulting in [$RHg^{\cdot}{}_{ads}$], but also from this radical to the starting cation (pathway *b*). This possibility follows from the acceleration of the electrochemical reaction, *i.e.*, the anomalously rapid disappearance of the starting compound from the solution. This pathway can result both in

RHg^{+}_{ads} and in free radical species, namely, $[RS^{\cdot}Me_2]$ and $R^{\cdot}$. These species can undergo subsequent reduction resulting in a significant increase in current, *i.e.*, in autocatalysis. An $R^{\cdot}$ species formed in the bulk of the solution can either undergo dimerization or accept an electron to give rise to an R^{-} anion. It is reasonable to assume that a significant amount of the β-regioisomer can be formed in this case. This mechanism explains the results obtained in run *1*, *i.e.*, the low overall yield of products **1a** and **1b** and the considerable amount of the β-isomer **1b** and dimer **1d**. Since pathway *b* cannot selectively give the target α-isoprenoid **1a**, it can be assumed that the factors that prevent the process from following pathway *b* should favor higher selectivity of the overall electrochemical process. Since pathway *b* is a bimolecular reaction, a decrease in the concentration of the starting sulfonium salt not only decreases the autocatalytic current but also increases the selectivity of the process. An analogous result is also attained by a purely technical procedure, *i.e.*, by displacement of the potential in the anodic direction (to $E \sim -0.6$ V) when autocatalysis starts. As a result, the reduction of the starting cation stops, the concentration of the $[RHg^{\cdot}_{ads}]$ species on the surface of the Hg electrode decreases, and hence the contribution of reactions *a* and *c* to the overall electrochemical process increases.

Pathway *a* (disproportionation) favors the selective formation of the target product. Probably, if a solvent containing 10 % H_2O is used, the process preferentially follows this pathway due to the rapid protonation of the R^{-} anion formed. The noticeable increase in the selectivity of the ER in run *3* (see Table 1) compared to run *2* becomes clear from this viewpoint.

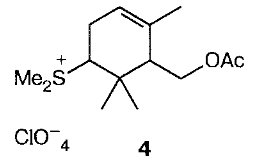
The third possible direction of the process is pathway *c*, according to which the $[RHg^{\cdot}_{ads}]$ radicals are transformed on the surface of the mercury cathode into "organic calomel"[13] or "organometal" type organomercury compounds, *i.e.*, compounds possessing electro-conducting crystalline structures,[14] which do not undergo reduction at −1.2 V. Electrolysis at more cathodic potentials results in reduction of $[RHg^{\cdot}_{ads}]$; as a consequence, the target α-isoprenoid **1a** is formed, and the equilibrium of reaction *c* is shifted to the right (Scheme 3). In our opinion, the high selectivity of the ER process results from the interaction of the allyl radical with the material of the cathode, *viz.*, mercury. The participation of mercury in the process considered indirectly follows from the formation of organomercury compounds in the ER of triphenyl-[15] and tribenzylsulfonium[16] salts (Ph_2Hg and $(PhCH_2)_2Hg$, respectively), although they were not isolated in the present study.

Scheme 3

$$[RHg^{\cdot}_{ads}]_x \overset{c}{\rightleftarrows} RHg^{\cdot}_{ads} \xrightarrow[E > -1.2\ V]{+e} RHg^{-} \xrightarrow[-Hg]{+DH} RH$$

Table 2 presents the maximum yields of the target products from salts **1**—**3** in DMF containing 10 % H_2O and 0.3 *M* $LiClO_4$ on a mercury cathode.

Conducting the ER of sulfonium salts **2** and **3** at more cathodic potentials than those indicated in Table 2 proved to be inefficient because the starting sulfonium salts obtained according to the procedure described previously[2] contained 10—15 % isomers (the cyclic isomer **4** in salt **3** and the β-regioisomer **5** in salt **2**), which are very difficult to separate.



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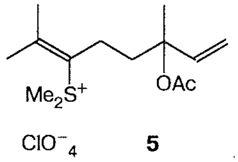


5

When salts **2** and **3** are reduced at more cathodic potentials, products of electrochemical and chemical transformations of the admixed sulfonium salts **4** and **5** appear in the reaction mixture. The latter salts do not undergo reduction below the potentials indicated in Table 2, which was confirmed by an ^1H NMR study of the reaction mixtures.

Since the ER of allyldimethylsulfonium salts is a two-step process,[10] we performed the electrolysis of salt **1** at the potential of the "second wave" ($E = -1.7$ V). The resulting complex mixture of products contained, in addition to the α- and β-isomers **1a** and **1b** (see Table 1, run *5*), side products, diastereomers of sulfide **1c** (yield ~15 %), whose structure was confirmed by spectral methods and by comparing it with the literature data,[2] and dimer **1d** (yield ~10 %). The presence of these products can be explained by the decomposition of the $[RS^{\cdot}Me_2]$ radical in the bulk of the solution (Scheme 4, pathway *a*). The preferential abstraction of the bulky allyl radical occurs because it is more stable than the methyl radical. The free allyl radical can readily undergo isomerization (into the corresponding β-isomer) and dimerization.

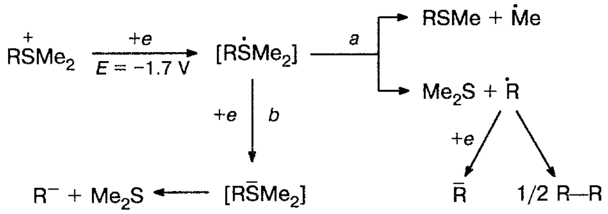
The change in the mechanism of the ER process from that occurring predominantly on the cathode surface at $E = -1.1$ V to the free-radical mechanism occurring in the bulk of the solution at $E = -1.7$ V is possible

Table 2. The yields of α-isoprenoids* **1a**—**3a** during the ER of allyldimethylsulfonium salts **1**—**3**

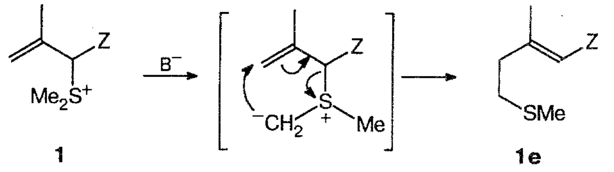
Sulfonium salt	E**/V	Yield*** (%)
1	−1.7	81
2	−1.5	66
3	−1.2	42

Note. Background solution: 0.3 *M* $LiClO_4$ in DMF—H_2O (9 : 1). * The content of β-isomers **1b**—**3b** does not exceed 5—10 %. ** The potential at the end of the ER. *** The yield of the products after distillation with respect to the starting amount of sulfonium salt.

Scheme 4



Scheme 5



B^- is a base

if the second-wave potential exceeds the potential of the desorption of the allyldimethylsulfonium salts studied [it should be noted that the desorption of tetraalkylammonium salts in aprotic solvents (DMSO, MeCN) is observed[17] at $E > -1.2$ V].

The mechanism proposed for the ER of salt **1** at the second-wave potential is supported by the fact that the ER of triphenyl-[15] and tribenzylsulfonium salts[16] gives organomercury compounds only when the electrolysis is carried out at the potential of the first wave.

In addition to the above pathway *a* (see Scheme 4), pathway *b*, which involves the subsequent reduction of the $[RS^{\cdot}Me_2]$ radical to form an anion followed by its decomposition, can also be proposed. Although this pathway can give the β-isomer, it cannot afford the dimer and the sulfide, RSMe.

When the concentration of salt **1** in the solution subjected to electrolysis is increased threefold (*cf.* runs *5* and *6*, Table 1), an even more complex mixture of products is formed. Separation on a column with SiO_2 gave three main fractions: a mixture of α- and β-isomers of **1a** and **1b** in the ratio 1 : 1, sulfides, and dimers.

As shown by chromatomass spectrometry, in addition to the expected diastereomers of sulfide **1c** with $[M]^+$ 244, the second fraction contains isomers with $[M]^+$ 258. The ^1H NMR spectrum contains, in addition to the signals of sulfides **1c**, additional signals, including those characteristic of the *E*/*Z*-MeC=CH moiety, namely, a broadened triplet and two singlets at δ 5.2, 1.7, and 1.6. Taken together, these data imply that sulfide **1e** described previously[2] is present in the mixture. This sulfide may originate from sulfonium salt **1** due to [3,2]-sigmatropic rearrangement induced by strong bases *via* an ylide (Scheme 5). Hence, one more side process occurs in dry DMF at $E = -1.7$ V with at least 0.03 *M* of the starting sulfonium salt **1**. This process related with ylide formation does not occur in any of the other cases considered.

The mass spectrum of the third fraction contains the molecular ion peak, $[M]^+$ 394, of dimer **1d** and the peaks of its most probable fragmentation products. On the other hand, the ^1H NMR spectrum contains the characteristic broadened signals of the isopropenyl moiety at δ 4.85, 4.75, and 1.65, in addition to the signals corresponding to dimer **1d**, which indicates that the mixture contains isomeric dimers.

Thus, we detected all of the most probable side products at the potential of the second wave of the ER of compound **1**. The formation of these products confirms that the process obeys the generally accepted mechanism,[3] according to which the cathode material is not very important.

To confirm the hypothesis concerning the decisive effect of the Hg-electrode on the selectivity of the ER of allyldimethylsulfonium salts, we made an attempt to reduce salt **1** in the bulk of the solution using the superoxide ion generated during the electrolysis of a sulfonium salt in the presence of O_2, as an electron carrier. The electrolysis was carried out at the potential of O_2 reduction (see Table 1, run *7*). As expected, no autocatalytic current increase was observed in this case. The electrolysis was not selective: the α- and β-isomers **1a** and **1b** predominate in the complex reaction mixture and all of the above side products and some unidentified products are present as well.

The results obtained by us indicate that the preparative ER of allyldimethylsulfonium salts is complicated by slow chemical transformations of the intermediates, which cannot be detected under the conditions of the polarographic experiment and therefore were not involved in the scheme of the process proposed previously.[10]

Thus, the highest yields of the target α-isoprenoids during the preparative electrolysis of allyldimethylsulfonium salts were obtained by direct ER on a mercury cathode in DMF—H_2O, 9 : 1 (using 0.3 *M* $LiClO_4$ as the background solution) with a gradual increase in potential from −1.1 to −1.7 V. It is desirable to use low concentrations of the starting salt or to introduce it gradually. The mechanism proposed for the preparative ER explains a number of anomalous phenomena observed during the electrolysis.

Experimental

IR spectra of the solutions were recorded on a UR-20 spectrophotometer. ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer; mass spectra were obtained on Varian MAT CH-6 and Varian MAT 311-A mass spectrometers with direct introduction of the sample or introduction through a chromatograph (a 3 m×3 mm column with 5 % SE-30 on Chromosorb W), electron impact energy 70 eV. GLC was performed on a LKhM-80 chromatograph equipped with a 2 m×3 mm column with 5 % OV-17 on Inerton AW-HMDS. The R_f values refer to a fixed layer of SiO_2 (Silufol) in an ether—hexane solvent system, 1 : 4.

Preparative electrolysis was performed under argon in a cell with a glass diaphragm using a P-5848 potentiostat. A mercury bottom cathode, a platinum net anode, and a saturated calomel reference electrode were used. Polarographic monitoring was performed using a PU-1 polarograph. Before distillation, DMF was dried with K_2CO_3 and 4 Å molecular sieves (after distillation dry DMF contained 0.2—0.3 % H_2O determined according to Fischer).

The perchlorates of (6-acetoxy-1-isopropenyl-4-methylhexyl)dimethylsulfonium (**1**), (4-acetoxy-1-isopropenyl-4-methyl-5-hexenyl)dimethylsulfonium (**2**), and (6-acetoxy-1-isopropenyl-4-methyl-4-hexenyl)dimethylsulfonium (**3**) were obtained by a known procedure.[2]

Acetate of 3,7-dimethyl-7-octen-1-ol (1a). A 0.05 *M* solution of sulfonium salt **1** (0.27 g) was electrolyzed at E_{init} = −1.1 V in 15 mL of 0.3 *M* $LiClO_4$ in DMF containing 10 % H_2O as the catholyte. As the current decreased, the potential was shifted to −1.7 V (electrolysis time 2 h, $Q \sim 2$ F mol^{-1}). When the electrolysis was completed, the solution was separated from the mercury. Water was added to the solution, which was then acidified with dilute HCl to pH 6 and extracted with ether. The extract was washed with water and dried with $MgSO_4$. The solution was concentrated *in vacuo*, and the residue (~0.15 g) was chromatographed on SiO_2 (30 g). Gradient elution from hexane to ether (up to 10 % of the latter) afforded 0.11 g (70 %) of compound **1a** as a colorless liquid with R_f 0.65. IR ($CHCl_3$), ν/cm^{-1}: 2980 and 2935 (C—H); 1730 (C=O); 1650 (C=C); 1215 (C(O)—O); 1050 (C—O); 720 (CH_2). ^1H NMR ($CDCl_3$), δ: 0.88 (d, 3 H, CH_3, *J* = 7 Hz); 1.1—1.7 (m, 7 H, CH, CH_2); 1.70 (br.s, 3 H, CH_3); 1.98 (br.t, 2 H, $CH_2C{=}C$, *J* = 8 Hz); 2.04 (s, 3 H, CH_3CO); 4.09 (m, 2 H, CH_2O); 4.68 and 4.64 (br.s, 2 H, $H_2C{=}C$). MS, *m/z*: 198 $[M]^+$, 138 $[M{-}AcOH]^+$, 123 $[M{-}AcOH{-}Me]^+$. For $C_{12}H_{22}O_2$: mol. weight 198.3.

In this series of experiments, the electrolyses were carried out as described above, at the potentials and H_2O content indicated in Table 1. The yields of product **1** were determined by GLC of the ethereal extracts of the reaction mixtures using naphthalene as the internal standard. The α/β isomeric ratio was determined by ^1H NMR after separation on a column with SiO_2.

The syntheses of α-isoprenoids **2a** and **3a** and their spectral characteristics have been reported previously.[1]

Diacetate of 3,7,10,14-tetramethylhexadeca-6,10*E*/*Z*-diene-1,16-diol (1d). A 0.1 *M* solution of sulfonium salt **1** (0.54 g) was electrolyzed at *E* = −1.25 V in 15 mL of 0.3 *M* $LiClO_4$ in dry DMF. When the electrolysis was completed, the solution was worked-up as described above, and the residue (~0.2 g) was chromatographed on a column with SiO_2 (30 g). Gradient elution from hexane to ether (up to 20 % of the latter) afforded 74 mg (25 %) of a mixture of α- and β-isoprenoids **1a** and **1b** (7 : 3 according to ^1H NMR data) and 30 mg (10 %) of dimer **1d** with R_f 0.38 as a colorless oil. For **1d**, IR ($CHCl_3$), ν/cm^{-1}: 2940 and 2970 (C—H); 1740 (C=O); 1250 (C(O)—O); 1035 and 1050 (C—O). ^1H NMR ($CDCl_3$), δ: 0.92 (br.d, 6 H, CH_3, *J* = 7 Hz); 1.2—1.75 (m, 10 H, CH, CH_2); 1.63 and 1.67 (br.s, 6 H, CH_3); 1.95—2.15 (m, 8 H, CH_2); 2.05 (s, 6 H, CH_3CO); 4.1 (m, 4 H, CH_2O); 5.1 (br.t, 2 H, HC=C). MS, *m/z*: 394 $[M]^+$, 334 $[M{-}AcOH]^+$, 319 $[M{-}AcOH{-}Me]^+$. For $C_{24}H_{42}O_4$: mol. weight 394.3.

Acetate of 3,7-dimethyl-6-methylthio-7-octen-1-ol (1c). A 0.01 *M* solution of sulfonium salt **1** (0.28 g) was electrolyzed at *E* = −1.7 V in 75 mL of 0.3 *M* $LiClO_4$ in dry DMF. When the electrolysis was completed, the solution was worked-up in the usual way, and the residue (~0.15 g) was chromatographed on a column with SiO_2 (30 g). Gradient elution from hexane to ether (up to 20 % of the latter) afforded 75 mg (50 %) of a mixture of α- and β-isomers **1a** and **1b** (1 : 1 according to ^1H NMR data), 28 mg (15 %) of a mixture of diastereomers of sulfide **1c** (R_f 0.52, colorless liquid) and 15 mg (10 %) of dimer **1d**, which was identical to the sample described above. For sulfide **1c**, IR ($CHCl_3$), ν/cm^{-1}: 2970 and 2940 (C—H); 1740 (C=O); 1250 (C(O)—O); 1035 and 1050 (C—O). ^1H NMR ($CDCl_3$), δ: 0.92 and 0.97 (d, 3 H, CH_3, *J* = 6.5 Hz); 1.1—1.8 (m, 7 H, CH, CH_2); 1.71 and 1.76 (br.s, 3 H, CH_3); 1.91, 1.93, 2.03, and 2.14 (s, 6 H, CH_3CO, CH_3S); 3.08 (m, 1 H, CHS); 4.10 (m, 2 H, CH_2O); 4.74 and 4.85 (br.s, 2 H, $C{=}CH_2$). MS, *m/z*: 244 $[M]^+$, 101 $[CH_2{=}C(CH_3)CH{-}SMe]^+$. For $C_{13}H_{24}O_2S$: mol. weight 244.2.

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