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Regioselective free radical phenylsulfenation of a non-activated δ-carbon atom by the photolysis of alkyl benzenesulfenate

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Abstract—A regioselective free radical introduction of a phenylthio group onto a non-activated δ-carbon atom was achieved by photolysis of alkyl benzenesulfenates in the presence of hexabutylditin, and δ-phenylthio alcohols were obtained in 35–91% yields. δ-Phenylsulfenylation of a non-activated carbon atom induced only by irradiation of alkyl benzenesulfenates (without initiation by hexabutylditin) also occurs, however, slower reaction rates were observed and lower yields of δ-phenylthio alcohols were obtained. © 2002 Published by Elsevier Science Ltd.

1. Introduction

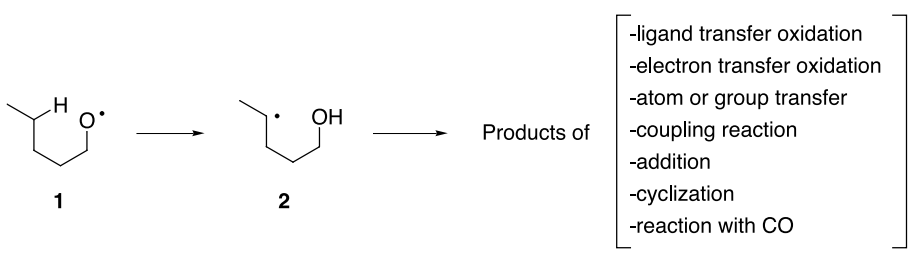
The introduction of various functional groups onto a remote, non-activated carbon atom is of great synthetic importance.[1] The regioselective functionalization of a non-activated δ-carbon atom involves a free radical 1,5-hydrogen migration from δ-carbon atom to oxygen[1a–e] **1** or nitrogen[1f,h] centered radicals and, thus, transposition of the radical center to δ-carbon atom **2** takes place. The reaction products and the nature of the introduced functional groups depend on the alkoxyl radical precursors and reagents used (Scheme 1).[2]

The carbon radicals generated by this methodology at an open chain, or fixed systems with suitable stereochemistry are preferentially located at the δ-position, although stereochemical circumstances determine the position of the hydrogen to be abstracted.[1a–e,3]

The reactivity of the δ-carbon radicals mainly depends on the RO· precursors, the reagents used, as well as the reaction conditions.[2,4] The reactivity of the carbon radical is determined by the rate of reaction with its radical counterpart, or added reagents, and also depends on the concentrations of the substrate and reagents used.[2g,h,5] In some of these reactions involving δ-carbon radicals **2**, generated by 1,5-transposition of the radical center, the carbon radical was intercepted by ligand[2h] or electron transfer oxidants,[2a,b,4d] atom or group transfer (formal substitution of the δ-hydrogen by an atom or group),[6] intermolecular addition,[7] cyclization[8] and reaction with carbon monoxide (Scheme 1).[9]

2. Results and discussion

Recently we found that δ-carbon radical **5**, formed by



Scheme 1.

Keywords: radicals and radical reactions; 1,5-hydrogen migration; intramolecular fuctionalization; sulfenic acids and derivatives; sulfides; δ-phenylthio alcohols.

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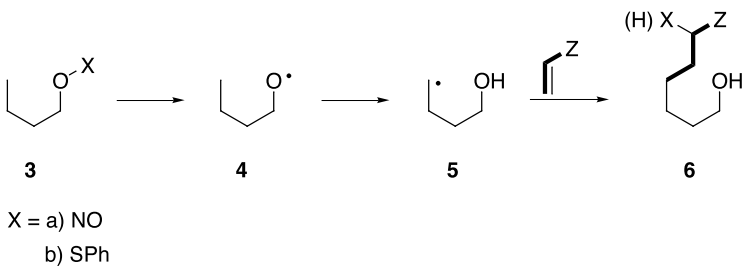
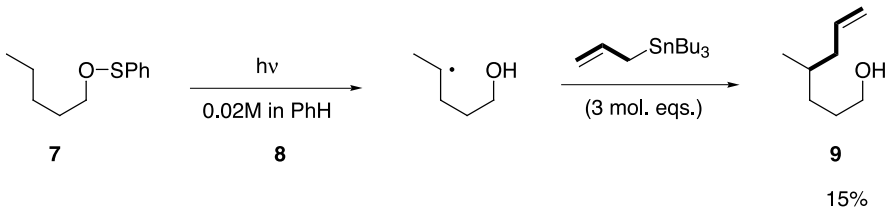
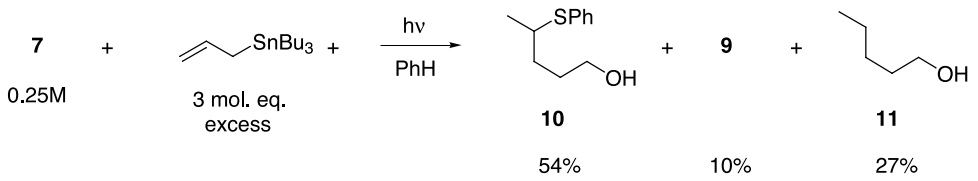


Scheme 2.



Scheme 3.



Scheme 4.

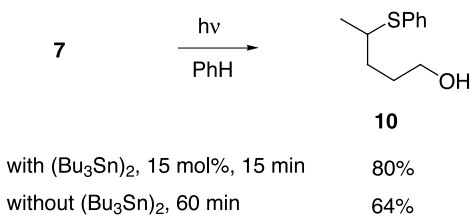
1,5-hydrogen migration in alkoxyl radical **4** was intercepted by radicophilic olefins, leading to Michael type alkylation of the remote non-activated carbon atoms.[7,9] δ-Alkylation was accomplished by the photolysis of alkyl nitrites **3a** or alkyl benzenesulfenates **3b** with tributyltin hydride (TBTH), both in the presence of an excess of electron deficient olefinic compound (Scheme 2).[10]

When 10 M equiv. of radicophilic olefin were used, the δ-alkyl radical **5**, generated by TBTH reduction of alkyl benzenesulfenates, preferentially underwent intermolecular addition ($K_{add}=3\times10^5\ M^{-1}\ s^{-1}$), rather than hydrogen transfer from TBTH ($K_H=2\times10^6\ M^{-1}\ s^{-1}$).[11]

In order to carry out allylation of the non-activated δ-carbon atom we envisioned to use allyltributyltin (ATBT) instead of TBTH.[12] Thus, in the reaction of *n*-pentyl benzenesulfenate **7** (0.02 M solution) with 3 M equiv. of allyltributyltin, under irradiation conditions, a low yield of unsaturated alcohol **9** was obtained as a product of the allylation of the δ-carbon atom (Scheme 3).

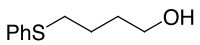
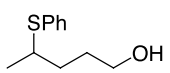
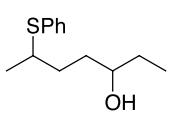
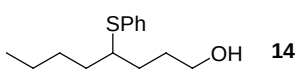
In order to increase the yield of the δ-allylated alcohol **9**, the concentration of *n*-pentyl benzenesulfenate was increased to 0.25 M solution, when only 10% of the δ-allylated product **9** was obtained. However, we isolated δ-phenylthio pentanol **10** as the main reaction product (Scheme 4).

Apparently, at this concentration, ATBT acted more as a sulfenation propagating species (via $Bu_3Sn^{\cdot}$) than as an allylating agent. Given the potential synthetic importance of



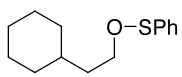
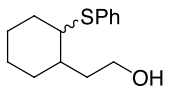
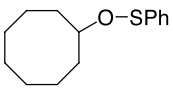
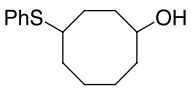
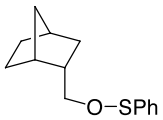
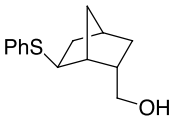
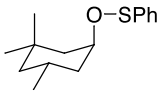
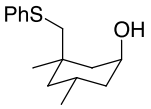
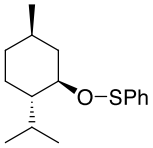
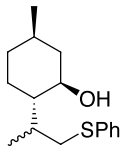
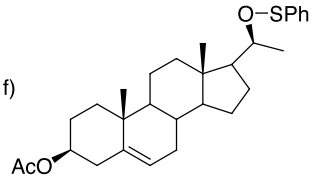
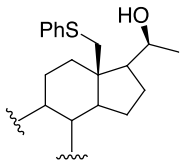
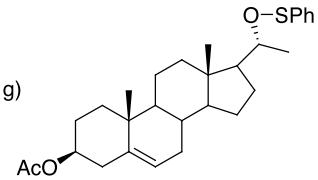
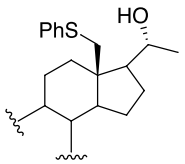
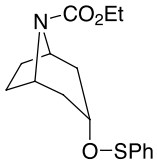
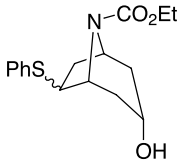
Scheme 5.

Table 1. Phenylsulfenylation of the non-activated δ-carbon atom by the photolysis of acyclic alkyl benzenesulfenates in the presence of hexabutylditin

Alkyl benzenesulfenates[a]	δ-Phenylthio alcohols		Yields (%)[b]
(a) *n*-Butyl		**12**	17
(b) 1-Pentyl		**10**	80[c]
(c) 3-Heptyl		**13**	91
(d) 1-Octyl		**14**	47

[a] Prepared according to the procedure described in Ref. 24.
[b] Isolated yields (GC yields are 10–20% higher).
[c] A 64% yield was obtained in the absence of $(Bu_3Sn)_2$.

Table 2. Phenylsulfenylation of non-activated δ-carbon atom by the photolysis of cyclic alkyl benzenesulfenates in the presence of hexabutylditin

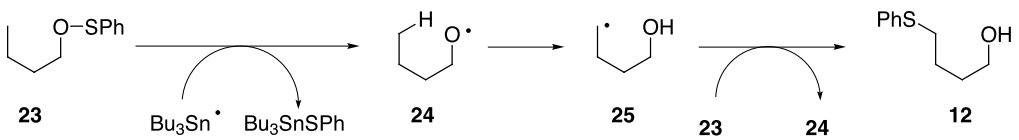
Alkyl benzenesulfenates[a]	δ-Phenylthio alcohols		Yields (%)[b]
a) 		**15**	51[c]
b) 		**16**	35
c) 		**17**	64[d]
d) 		**18**	62
e) 		**19**	43[e]
f) 		**20**	40
g) 		**21**	40
h) 		**22**	45[f]

[a] Prepared according to procedure described in Ref. 24.
[b] Isolated yields (GC yields are 10–20% higher).
[c] The ratio of *trans*/*cis*=1:0.86.
[d] Only the *exo*-isomer was obtained.
[e] (−)-(1*R*,3*R*,4*S*,8*S*)-**19a** and (−)-(1*R*,3*R*,4*S*,8*R*)-Menthane-3-9-diol-**19b** were obtained in the ratio of 10.5:1.
[f] The ratio of *exo*/*endo*=2:1.

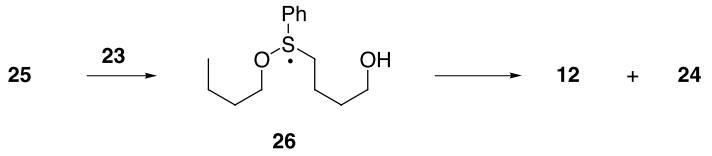
a new, general method for δ-phenylsulfenylation we set out to further optimize the reaction conditions for this transformation. Substituting hexabutylditin for ATBT resulted in a yield enhancement, and δ-phenylthio pentanol **10** was obtained in 80% yield.[13] However, although a tinless variant of the sulfenylation reaction would also be conceivable, in the absence of hexabutylditin the reaction proceeded at a lower rate (60 min), and gave a lower yield of δ-phenylthio pentanol (Scheme 5).

Phenylsulfenylation of the non-activated δ-carbon atom was applied in various structurally related alcohols. The results obtained using acyclic alkyl benzenesulfenates are presented in Table 1, while the phenylthio alcohols obtained from cyclic alkyl benzenesulfenates are summarized in Table 2.

This type of free radical phenylthio group transfer essentially represents a simple interchange of the positions



Scheme 6.



Scheme 7.

of hydrogen and phenylthio groups. The sequence of radical reactions is initiated by the tributyltin radical and is based on its thiophilic addition to the sulfur of alkyl benzenesulfenate. The formed alkoxyl radical **24** upon intramolecular 1,5-hydrogen migration, gives the δ-carbon radical **25** (Scheme 6).

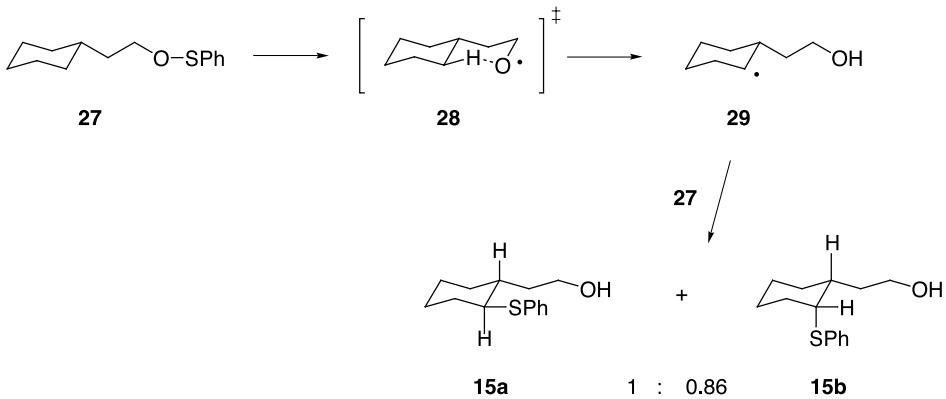
In the absence of any other reactive species the carbon radical **25** undergoes homolytic substitution at the sulfur in the alkyl benzenesulfenate **23**, involving the intermediary hypervalent sulfuranyl radical **26**. A substitution at sulfur involves the S–O bond cleavage with formation of δ-phenylthio alcohol **12**, as a final reaction product, and generating the alkoxyl radical **24** as a transient radical which continues the chain (Scheme 7).[14]

Comparable results for δ-phenylsulfenylation were obtained when irradiation of *n*-pentyl benzenesulfenates was carried out without hexabutylditin, when δ-phenylthio pentanol was obtained in 64% yield. This result indicates that the alkoxyl radical **24** is generated by photo-induced homolytic dissociation of alkyl benzenesulfenates[6] and δ-phenylsulfenylation occurs as in the presence of tributyltin radical as an initiator.

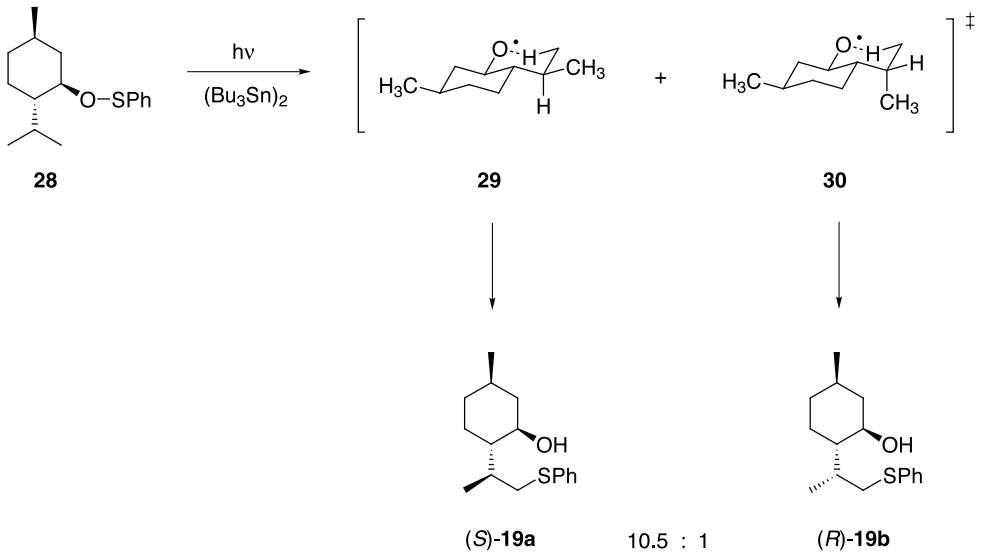
Remote phenylsulfenylation of the cyclohexane ring is not stereoselective. Thus in the reaction of cyclohexylethyl benzenesulfenate (**27**), phenylthio group transfer from the side-chain onto the cyclohexane ring takes place and a mixture of *cis*- and *trans*-2-phenylthiocyclohexyl ethanol was obtained in the ratio of *trans*/*cis*=1:0.86. Although the *trans*-isomer **15a** is more stable for steric reasons, its formation, involving the intermediate **26** requires a non-favorable equatorial approach of the cyclohexyl radical to the starting compound. On the other hand, axial attack of the cyclohexyl radical **29** onto the alkyl benzenesulfenate, leading to an axial phenylthio group is more favorable, although the less stable *cis*-isomer **15b** is formed (Scheme 8).[15] These two factors probably determine the distribution of stereoisomers **15a** and **15b**. The ratio of *cis*- and *trans*-isomers was determined by ^{1}H NMR spectrum of the mixture of **15a** and **15b**.[16]

However, the δ-phenylsulfenylation of *endo*-2-norbornylmethyl benzenesulfenate proceeds stereoselectively and only *exo*-6-phenylthio-*endo*-2-norbornylmethanol **17** was obtained. This result is in agreement with stereoselective reaction of the norbornyl radical proceeding with an *exo*-approach to the alkyl benzenesulfenate.[17]

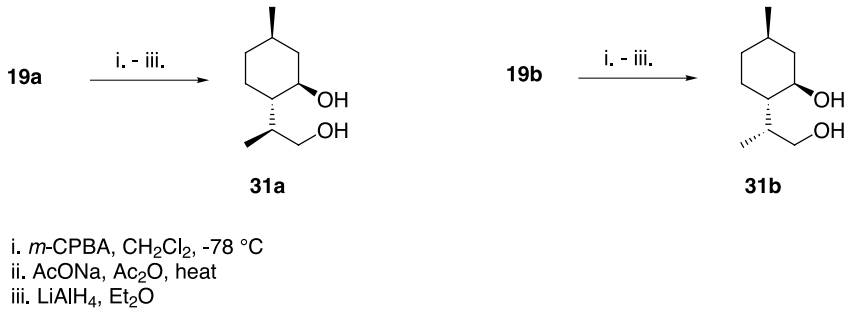
An interesting stereoselectivity of the δ-phenylsulfenylation reaction was achieved in the photolysis of (−)-menthyl benzenesulfenate. It should be expected that the two non-activated methyl groups to be attacked are equivalent for introduction of the phenylthio group, since the rotational barrier for the isopropyl group is relatively low. However, it was found that this reaction proceeds stereoselectively and two stereoisomers **19a** (*S*)- and **19b** (*R*)- were obtained in the ratio 10.5:1 (Scheme 9). Two stereoisomers were separated by chromatography. The formation of the *S*-diastereoisomer **19a** in a considerable excess may be explained by the different stereochemical interactions in the



Scheme 8.



Scheme 9.

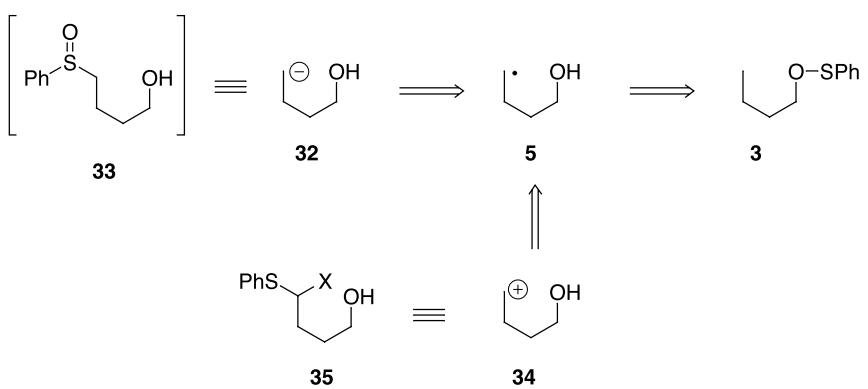


Scheme 10.

transition states necessary for 1,5-hydrogen migration and the generation of two diastereoisomeric carbon radicals. In the six-membered transition state **29**, leading to *S*-diastereoisomer **19a**, the non-reacting methyl group (from the isopropyl group) is in a quasi-equatorial position, while in the transition state **30**, leading to the *R*-diastereoisomer **19b**, the methyl group is in the less favorable quasi-axial position.

The absolute configurations of **19a** and **19b** were confirmed by their transformation to the corresponding diastereomeric menthane-3,9-diols **31a** and **31b** the stereochemistry of which was determined by Ohloff.[18] The separated diastereomeric phenylthio alcohols **19a** and **19b** were subjected to the following sequence of reactions: oxidation by *m*-CPBA to the correspondig sulfoxides,[19] Pummerer rearrangement[20] and reduction of isomeric α-acetoxy sulfides with $LiAlH_4$; thus the (−)-(1*R*,3*R*,4*S*,8*S*)-menthane-3,9-diol **31a** and (−)-(1*R*,3*R*,4*S*,8*R*)-menthane-3,9-diol **31b** were obtained (Scheme 10). Physical constants and spectral evidence were in full agreement with the corresponding stereoisomers independently prepared from the (−)-isopulegol by the previously described procedure.[18]

Introduction of the phenylthio group onto the non-activated δ-carbon atom of alcohols can have valuable synthetic



Scheme 11.

applications. For example, δ-phenylthio alcohols derived from radical **5** may be easily oxidized to the corresponding δ-sulfoxides **33** and δ-sulfones[21] with their versatile reactivities, or they can be deprotonated by a strong base, and convert the δ-carbon atom to the nucleophilic species **32**.[22] Conversion of the activated δ-carbon atom of the δ-phenylthio alcohols to the carbonyl group can be achieved via halogenation (**35**)[23] followed by subsequent hydrolysis to the corresponding carbonyl compounds. In this way an inversion of the reactivity of the δ-carbon atom, may be accomplished and it can react as an electron acceptor **34** (Scheme 11).

3. Experimental

Solvents used in all of the experiments were purified by distillation before use (benzene distilled over calcium hydride and methylene chloride over phosphorous pentoxide). Petroleum ether refers to the fraction with distillation range 45–65°C. Purification and separation of the reaction products were carried out by distillation and column chromatography using silica gel 100–200 mesh (60 Å) and by dry flash chromatography using silica gel (60 Å). The reactions were monitored by TLC using silica gel (TLC 60 Å) or by GC (Varian 3400, column OV-101 1% on Chromosorb W-AW). IR spectra (ν_{max} in cm^{-1}) were recorded on Perkin–Elmer 457 grating instrument. ^1H NMR spectra (ppm in δ-values) were recorded (in $CDCl_3$) at 200 MHz, using Varian Gemini 200. ^{13}C NMR spectra were recorded on the same instrument at 50 MHz. Mass spectra were recorded on Finningan ITDS 700 instrument.

3.1. Synthesis of alkyl benzenesulfenates

General procedure.[24] To the solution of alcohol (0.02 mol) and triethylamine (0.05 mol) in methylene chloride (150 mL), cooled to −78°C under an argon atmosphere, benzenesulfenyl chloride (0.025 mL) was added during 10 min at −78°C and left to reach rt. The mixture was diluted with 400 mL of methylene chloride and washed successively with 50 mL of 2 M hydrochloric acid, 50 mL of saturated aqueous sodium bicarbonate and water. The solution was dried over sodium sulfate. Solvent was removed by evaporation and residual oil distilled on a short path under reduced pressure. Solid alkyl benzenesulfenates were purified by dry flash chromatography. Alkyl benzenesulfenates were obtained in 65–87% yields.

3.1.1. *n*-Butyl benzenesulfenate. 65% Yield, yellow-green liquid, bp 74–76°C/0.22 mm Hg. IR (neat, cm^{-1}): 3059, 2000–1600, 1584, 1478, 1439, 1378, 1121, 1090, 1059, 1024, 995, 965, 943, 903, 860, 773, 738, 691. ^1H NMR (200 MHz) δ: 0.90 (t, *J*=7.4 Hz, 3H), 1.36 sext, *J*=7.4 Hz, 2H), 1.57–1.71 (m, 2H), 3.80 (t, *J*=6.8 Hz, 2H), 7.12–7.40 (m, 5H). ^{13}C NMR (50 MHz) δ: 140.83, 128.80, 126.19, 123.46, 78.20, 32.30, 18.83, 13.62.

3.1.2. *n*-Pentyl benzenesulfenate. 73% Yield, yellow-green oil, bp 70°C/0.1 mm Hg. Anal. calcd $C_{11}H_{16}OS$: C, 67.30; H, 8.22; S, 16.33. Found: C, 67.72; H, 8.23; S, 16.43. IR (neat, cm^{-1}): 3060, 2000–1600, 1583, 1477, 1439, 1378, 1300, 1089, 1069, 1043, 1024, 970, 892, 807, 738, 691. ^1H NMR (200 MHz) δ: 0.86–0.93 (m, 3H), 1.26–1.38 (m, 4H), 1.60–1.70 (m, 2H), 3.81 (t, *J*=6.6 Hz, 2H), 7.14–7.42 (m, 5H). ^{13}C NMR (50 MHz) δ: 140.82, 128.74, 126.11, 78.40, 29.92, 27.71, 22.23, 13.78.

3.1.3. 3-Heptyl benzenesulfenate. 78% Yield, yellow-green oil, bp 86–89°C/0.3 mm Hg. IR (neat, cm^{-1}): 3061, 2000–1600, 1584, 1477, 1465, 1439, 1113, 1068, 1024, 944, 916, 893, 811, 738, 690. ^1H NMR (200 MHz) δ: 0.88 (t, *J*=6.4 Hz, 6H), 1.20–1.37 (m, 4H), 1.53–1.72 (m, 4H), 3.52 (quint, *J*=5.8 Hz, 1H), 7.14–7.36 (m, 5H). ^{13}C NMR (50 MHz) δ: 141.38, 128.62, 126.38, 124.53, 88.67, 32.95, 27.07, 26.44, 22.61, 13.87, 9.15.

3.1.4. *n*-Octyl benzenesulfenate. 71% Yield, yellow-green oil, bp 103–105°C/0.02 mm Hg. IR (neat, cm^{-1}): 3060, 2000–1600, 1583, 1478, 1440, 1378, 1148, 1068, 1024, 968, 894, 737, 690. ^1H NMR (200 MHz) δ: 0.88 (t, *J*=6.2 Hz, 3H), 1.20–1.40 (m, 10H), 1.58–1.73 (m, 2H), 3.80 (t, *J*=6.6 Hz, 2H), 7.13–7.40 (m, 5H). ^{13}C NMR (50 MHz) δ: 140.85, 128.87, 126.28, 123.57, 78.62, 31.70, 30.32, 29.12, 25.66, 22.56, 14.02.

3.1.5. 2-(Cyclohexyl)-ethyl benzenesulfenate. 84% Yield, yellow-green oil, bp 110–112°C/0.05 mm Hg. IR (neat, cm^{-1}): 3059, 2000–1600, 1583, 1477, 1448, 1440, 1378, 1090, 1067, 1024, 998, 971, 891, 835, 737, 690. ^1H NMR (200 MHz) δ: 0.80–0.94 (m, 2H), 1.10–1.45 (m, 4H), 1.53 (q, *J*=6.6 Hz, 2H), 1.55–1.70 (m, 5H), 3.82 (t, *J*=6.6 Hz, 2H), 7.10–7.35 (m, 5H). ^{13}C NMR (50 MHz) δ: 140.79, 128.76, 126.19, 123.55, 76.49, 37.67, 34.09, 33.07, 26.35, 26.06.

3.1.6. *trans*-3,3,5-Trimethylcyclohexyl benzenesulfenate. 77% Yield, yellow-green oil, bp 102–104°C/0.09 mm Hg. IR (neat, cm^{-1}): 3060, 2000–1600, 1584, 1477, 1455, 1439, 1387, 1364, 1344, 1247, 1180, 1154, 1091, 1077, 1068, 1024, 988, 926, 911, 884, 834, 737, 690. ^1H NMR (200 MHz) δ: 0.87 (d, *J*=7.2 Hz, 3H), 0.89 (s, 3H), 1.08 (s, 3H), 0.74–1.21 (m, 3H), 1.37–1.55 (m, 1H), 1.86–2.12 (m, 3H), 3.86 (quint, *J*=3.0 Hz, 1H), 7.09–7.39 (m, 5H). ^{13}C NMR (50 MHz) δ: 141.50, 128.78, 125.75, 122.76, 83.30, 48.23, 41.63, 39.03, 33.91, 30.53, 27.51, 22.83, 22.41.

3.1.7. Cyclooctyl benzenesulfenate. 77% Yield, yellow-green oil, bp 120–122°C/0.3 mm Hg. IR (neat, cm^{-1}): 3059, 2000–1600, 1582, 1477, 1440, 1362, 1329, 1148, 1086, 1068, 1046, 1024, 940, 912, 884, 844, 771, 737, 690. ^1H NMR (200 MHz) δ: 1.30–2.10 (m, 14H), 3.60–3.75 (m, 1H), 7.05–7.40 (m, 5H). ^{13}C NMR (50 MHz) δ: 141.90, 128.77, 125.68, 122.02, 88.24, 31.94, 27.13, 25.19, 22.86.

3.1.8. *endo*-2-Norbornylmethyl benzenesulfenate. 84% Yield, bp 115°C/0.04 mm Hg. IR (neat, cm^{-1}): 3059, 2000–1600, 1582, 1478, 1452, 1440, 1379, 1344, 1301, 1171, 1135, 1068, 1041, 1024, 974, 954, 929, 779, 738, 690. ^1H NMR (200 MHz) δ: 0.55–0.65 (m, 1H), 0.95–1.76 (m, 8H), 2.17–2.29 (m, 2H), 3.74–3.79 (m, 2H), 7.13–7.45 (m, 5H). ^{13}C NMR (50 MHz) δ: 140.87, 128.88, 126.36, 123.74, 80.85, 40.44, 39.64, 38.14, 36.55, 33.59, 29.76, 22.61.

3.1.9. (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl benzenesulfenate [(−)-menthyl benzenesulfenate]. 87%

Yield, yellow-green oil, bp 108–110°C/0.07 mm Hg. Micro analysis was not performed because the compound decomposes with explosion in the Pregl apparatus, $[\alpha]_D^{22}=-256.7$ (c=1, $CHCl_3$) of 92% purity of compound (determined by ^{1}H NMR spectrum). IR (neat, cm^{-1}): 3062, 2000–1600, 1583, 1477, 1455, 1440, 1387, 1370, 1345, 1097, 1024, 1004, 981, 959, 914, 851, 778, 738, 690. ^{1}H NMR (200 MHz) δ: 0.62 (d, J=7.0 Hz, 3H), 0.87 (d, J=7.2 Hz, 3H), 0.88 (d, J=7.2 Hz, 3H), 0.72–1.00 (m, 3H), 1.20–1.38 (m, 2H), 1.54–1.66 (m, 2H), 2.18–2.38 (m, 2H), 3.37 (td, J_1=10.7 Hz, J_2=4.4 Hz, 1H), 7.10–7.40 (m, 5H). ^{13}C NMR (50 MHz) δ: 141.29, 128.52, 126.65, 125.37, 87.01, 48.62, 40.88, 34.10, 31.50, 25.06, 22.93, 22.03, 20.87, 15.59.

3.1.10. *N*-Carbethoxy nortropine-3α-benzenesulfenate. 97% Yield, yellow-green crystals, mp 45°C. Anal. calcd $C_{16}H_{21}NO_3S$: C, 62.54; H, 6.84; N, 4.56. Found: C, 62.68, H, 7.05, N, 4.42. IR (KBr, cm^{-1}): 2000–1800, 1696, 1583, 1477, 1439, 1383, 1354, 1325, 1314, 1225, 1212, 1169, 1107, 1032. ^{1}H NMR (200 MHz) δ: 1.23 (t, J=7.0 Hz, 3H), 1.89–2.13 (m, 8H), 3.74–3.82 (m, 1H), 4.11 (q, J=7.0 Hz, 2H), 4.17–4.30 (m, 2H), 7.11–7.40 (m, 5H). ^{13}C NMR (50 MHz) δ: 153.67, 140.05, 128.92, 126.43, 123.74, 80.00, 60.70, 52.15, 36.13, 35.53, 28.24, 27.61, 14.64. MS (CI): 308 (M^++1) 100%, 183 [(M^++1)–OSPh] 50%.

3.1.11. 3β-Acetoxy-5-pregnen-20β-yl benzenesulfenate. 48% Yield, pale yellow crystals, IR (KBr, cm^{-1}): 3074, 2000–1600, 1732, 1584, 1477, 1438, 1370, 1332, 1249, 1198, 1146, 1134, 1119, 1091, 1072, 1039, 1011, 959, 931, 902, 891, 881, 865, 803, 772, 731, 688. ^{1}H NMR (200 MHz) δ: 0.59 (s, 3H), 1.02 (s, 3H), 1.16 (d, J=6.2 Hz, 3H), 0.92–1.32 (m, 7H), 1.37–1.67 (m, 8H), 1.69–1.91 (m, 2H), 2.03 (s, 3H), 2.08–2.15 (m, 1H), 2.29–2.34 (m, 2H), 3.69–3.80 (m, 1H), 4.58–4.63 (m, 1H), 5.36 (d, J=4.4 Hz, 1H), 7.17–7.46 (m, 5H). ^{13}C NMR (50 MHz) δ: 170.51, 141.20, 139.73, 128.61, 127.09, 126.59, 122.40, 86.36, 73.89, 56.58, 55.97, 49.94, 42.09, 39.09, 38.04, 36.90, 36.54, 31.80, 31.66, 27.66, 25.65, 24.30, 21.37, 20.77, 19.44, 19.26, 12.03.

3.1.12. 3β-Acetoxy-5-pregnen-20α-yl benzenesulfenate. 54% Yield, pale yellow crystals, IR (KBr, cm^{-1}): 3054, 2000–1600, 1731, 1581, 1472, 1441, 1372, 1330, 1245, 1195, 1146, 1132, 1114, 1102, 1070, 1030, 1010, 954, 929, 900, 865, 744, 691. ^{1}H NMR (200 MHz) δ: 0.59 (s, 3H), 0.99 (s, 3H), 1.30 (d, J=6.0 Hz, 3H), 0.92–1.32 (m, 7H), 1.37–1.67 (m, 8H), 1.83–1.92 (m, 2H), 2.03 (s, 3H), 2.08–2.15 (m, 1H), 2.29–2.34 (m, 2H), 3.50–3.64 (m, 1H), 4.50–4.68 (m, 1H), 5.37 (d, J=4.8 Hz, 1H), 7.17–7.49 (m, 5H). ^{13}C NMR (50 MHz) δ: 170.54, 141.51, 139.57, 128.65, 126.58, 125.09, 122.49, 87.85, 73.85, 56.82, 56.39, 49.79, 41.85, 38.63, 38.01, 36.90, 36.49, 31.75, 31.50, 27.66, 25.62, 24.12, 21.37, 20.65, 20.10, 19.22, 12.24.

3.2. Phenylsulfenylation of non-activated δ-carbon atom by photolysis of alkyl benzenesulfenates in the presence of hexabutylditin

General procedure. A solution of 0.5 mmol of alkyl benzenesulfenate and 0.07 mmol (40 mg) of hexabutylditin in 2 mL of benzene was irradiated at rt, in an argon atmosphere, by a 125 W high pressure mercury lamp during 15 min. Benzene was removed by evaporation and the reaction products from an oily residue were separated by chromatography on silica gel column using petrolether/aceton 95:5 or 90:10.

3.2.1. 4-Phenylthio-1-butanol (12). A solution of of *n*-butyl benzenesulfenate (0.091 g, 0.5 mmol) and hexabutylditin (0.040 g, 0.07 mmol) in benzene (2 mL) was irradiated according to general procedure. 4-Phenylthio-1-butanol was isolated by column chromatography in 17% (15 mg) as a colorless oil. IR (neat, cm^{-1}): 3381, 2000–1600, 1584, 1481, 1439, 1062, 1026, 739, 691. ^{1}H NMR (200 MHz) δ: 1.67–1.76 (m, 4H), 2.96 (t, J=7.0 Hz, 2H), 3.66 (t, J=6.0 Hz, 2H) 7.10–7.40 (m, 5H). ^{13}C NMR (50 MHz) δ: 136.57, 129.12, 128.88, 125.86, 62.34, 33.43, 31.67, 25.45. HRMS calcd for $C_{10}H_{14}OS$ (M^+): 182.0765. Found: 182.0767.

3.2.2. 4-Phenylthio-1-pentanol (10). Obtained from *n*-pentyl benzenesulfenate in 80% yield, isolated as a colorless liquid. IR (neat, cm^{-1}): 3385, 2000–1600, 1584, 1480, 1439, 1404, 1377, 1263, 1092, 1065, 1025, 910, 739, 693. ^{1}H NMR (200 MHz) δ: 1.29 (d, J=6.8 Hz, 3H), 1.56–1.78 (m, 5H), 3.25 (sext, J=6.6 Hz, 1H), 3.64 (t, J=6.2 Hz, 1H), 7.17–7.33 (m, 3H) 7.36–7.43 (m, 2H). ^{13}C NMR (50 MHz) δ: 135.09, 132.00, 128.79, 126.75, 62.61, 43.14, 32.75, 30.04, 21.15. HRMS calcd for $C_{11}H_{16}OS$ (M^+): 196.0922. Found: 196.0924.By photolysis of *n*-pentyl benzenesulfenate in benzene solution in the absence of hexabutylditin for 1 h, 4-phenylthio-1-pentanol (**10**) was obtained in 64% yield.

3.2.3. 4-Phenylthio-1-octanol (14). The title compound was isolated as a colorless oil in 47% yield. Anal. calcd $C_{14}H_{22}OS$: C, 70.54; H, 9.30; S, 13.45. Found: C, 70.32; H, 9.46; S, 13.45. IR (neat, cm^{-1}): 3348, 2000–1600, 1584, 1479, 1467, 1455, 1439, 1379, 1306, 1091, 1065, 1026, 745, 693. ^{1}H NMR (200 MHz) δ: 0.88 (t, J=7.1 Hz, 3H), 1.24–1.84 (m, 10H), 3.10 (quin, J=6.6 Hz, 1H), 3.58–3.68 (m, 2H), 7.20–7.45 (m, 5H). ^{13}C NMR (50 MHz) δ: 135.49, 131.86, 128.76, 126.59, 62.67, 48.90, 34.21, 30.61, 29.75, 28.86, 22.51, 13.92. MS (CI): 239 (M^++1) 100% (exact mass: 238.14; mol. wt: 238.39).

3.2.4. 2-Phenylthio-5-heptanol (13). In the photolysis of 3-heptyl benzenesulfenate (0.11 g, 0.5 mmol) in the presence of hexabutylditin, the title compound was isolated as a colorless oil (0.1 g, 91% yield) and a mixture of two diastereoisomers (1:1) was obtained. Anal. calcd $C_{13}H_{20}OS$: C, 69.59; H, 8.98; S, 14.29. Found: C, 69.44; H, 9.07; S, 14.33. IR (neat, cm^{-1}): 3413, 3075 2000–1600, 1585, 1480, 1457, 1439, 1377, 1303, 1263, 1217, 1093, 1069, 1026, 1000, 971, 910, 759, 693. ^{1}H NMR (200 MHz) δ: 0.93 (t, J=7.4 Hz, 3H), 1.30 (d, J=6.6 Hz, 3H), 1.40–1.80 (m, 6H), 3.13–3.30 (m, 1H), 3.45–3.57 (m, 1H), 7.20–7.35 (m, 3H), 7.36–7.46 (m, 2H). ^{13}C NMR (50 MHz) δ: 135.17, 131.10, 128.78, 126.66, 73.04, 72.95, 43.40, 43.29, 34.16, 33.91, 32.65, 32.43, 30.15, 30.07, 21.16, 9.77. MS (CI): 225 (M^++1) 100%, 207 [(M^++1)–H_2O] 50% (exact mass: 224.12; mol. wt: 224.36).

3.2.5. *cis*- and *trans*-2-(2-Phenylthiocyclohexyl)-ethanol (15). This compound was obtained in 51% yield from

2-(cyclohexyl)-ethyl benzenesulfenate. The title compound was isolated as a colorless oil and contains *cis*- **15b** and *trans*-isomer **15a** in ratio of 0.86:1. Anal. calcd $C_{14}H_{20}OS$: C, 71.14; H, 8.53; S, 13.57. Found: C, 71.00; H, 8.70; S, 13.30. IR (neat, cm^{-1}): 3335, 2000–1600, 1584, 1479, 1439, 1350, 1271, 1088, 1068, 1048, 1026, 1008, 974, 901, 749, 692. ^1H NMR (200 MHz) δ: 1.00–2.10 (m, 11.46H), 2.26 (dt, J_1=10.6 Hz, J_2=7.4 Hz, 0.54H), 2.84 (td, J_{aa}=10.1 Hz, J_{ae}=3.6 Hz, 0.54H), 3.50 (td, J_{ee}=4.4 Hz, J_{ae}=3.4 Hz, 0.46H), 3.62–3.82 (m, 2H), 7.15–7, 48 (m, 5H). ^{13}C NMR (50 MHz) δ: 136.30, 135.09, 132.22, 131.34, 128.81, 128.72, 126.68, 126.32, 60.67, 52.64, 51.65, 38.84, 37.29, 37.11, 35.76, 34.16, 32.10, 31.03, 28.62, 26.07, 25.24, 24.73, 21.91. MS (CI): 237 (M^++1) 100% (exact mass: 236.12; mol. wt: 236.37).

3.2.6. 4-Phenylthiocyclooctanol (16). The title compound was obtained (from cyclooctyl benzenesulfenate, 0.12 g, 0.5 mmol) as a mixture of *cis*- and *trans*-isomers and isolated (40 mg, 35% yield) as colorless oil. IR (neat, cm^{-1}): 3353, 2000–1600, 1584, 1475, 1439, 1365, 1275, 1238, 1146, 1091, 1068, 1045, 1026, 1000, 910, 750, 737, 692. ^1H NMR (200 MHz) δ: 1.25–2.20 (m, 13H), 3.25–3.45 (m, 1H), 3.80–3.95 (m, 1H), 7.20–7.45 (m, 5H). ^{13}C NMR (50 MHz) δ: 135.59, 131.90, 131.75, 128.85, 126.73, 126.68, 71.77, 71.44, 48.13, 47.99, 34.13, 33.87, 32.81, 32.55, 30.40, 30.27, 27.66, 27.62, 25.28, 25.03, 22.71, 22.07. HRMS calcd for $C_{14}H_{20}OS$ (M^+): 236.1235. Found: 236.1239.

3.2.7. *endo*-2-Hydroxymethyl-*exo*-6-phenylthio-norbornane (17). The title compound was obtained as colorless oil in 64% yield, from *endo*-2-norbornyl benzenesulfenate according to the general procedure. IR (neat, cm^{-1}): 3362, 2000–1600, 1585, 1483, 1439, 1353, 1326, 1305, 1285, 1268, 1094, 1068, 1044, 1017, 975, 898, 734, 693. ^1H NMR (200 MHz) δ: 0.67 (ddd, J_1=12.4 Hz, J_2=5.3 Hz, J_3=2.6 Hz, 1H), 1.25–1.38 (m, 2H), 1.43–1.59 (m, 1H), 1.68–1.86 (m, 3H), 2.12–2.42 (m, 3H), 3.56 (ddd, J_1=8.4 Hz, J_2=4.3 Hz, J_3=1.6 Hz, 1H), 3.60–3.78 (m, 2H), 7.10–7.40 (m, 5H). ^{13}C NMR (50 MHz) δ: 137.68, 128.79, 128, 40, 125.43, 63.93, 43.87, 42.34, 41.42, 38.88, 37.12, 36.73, 32.33. HRMS calcd for $C_{14}H_{18}OS$ (M^+): 234.1078. Found: 234.1082.

3.2.8. *endo*-2-Acetoxymethyl-*exo*-6-phenylthio-norbornane. This compound was prepared in order to confirm the *exo* orientation of the phenylthio group in *endo*-2-hydroxymethyl-6-phenylthio-norbornane. Colorless oil, IR (neat, cm^{-1}): 2000–1600, 1749, 1586, 1464, 1378, 1301, 1235, 1122, 1040, 798, 736, 690. ^1H NMR (200 MHz) δ: 0.70 (ddd, J_1=12.2 Hz, J_2=5.2 Hz, J_3=2.6 Hz, 1H), 1.25–1.38 (m, 2H), 1.70–1.87 (m, 3H), 1.99 (s, 3H), 2.21–2.35 (m, 3H), 3.50 (ddd, J_1=8.3 Hz, J_2=4.5 Hz, J_3=1.6 Hz, 1H), 3.92 (dd, J_{gem}=11.0 Hz, J_{vic}=10.6 Hz, 1H), 4.22 (dd, J_{gem}=11.0 Hz, J_{vic}=6.6 Hz, 1H), 7.10–7.40 (m, 5H). ^{13}C NMR (50 Hz) δ: 171.02, 137.40, 129.19, 128.76, 125.76, 65.05, 44.01, 41.83, 38.57, 38.46, 36.92, 36.67, 32.27, 20.86. HRMS calcd for $C_{16}H_{20}O_2S$ (M^+): 276.1184. Found: 276.1187.

3.2.9. (−)-(1*R*,2*S*,5*R*,1′*S*)-5-Methyl-2-(1-methyl-2-phenylthio-ethyl)-cyclohexanol [(−)-(1*R*,3*R*,4*S*,8*S*)-9-phenylthiomenthol] (19a). The title compound was obtained as a white crystalline compound, mp 49°C, $[\alpha]_D^{21}$=−29.4 (c=1, $CHCl_3$), in 39% yield by photolysis of (−)-menthyl benzenesulfenate according to the described procedure. Anal. calcd $C_{16}H_{24}OS$: C, 72.67; H, 9.15; S, 12.13. Found: C, 72.72; H, 9.33; S, 12.41. IR (neat, cm^{-1}): 3392, 2000–1600, 1584, 1480, 1455, 1439, 1377, 1312, 1263, 1147, 1091, 1049, 1026, 991, 965, 922, 885, 846, 737, 691. ^1H NMR (200 MHz) δ: 0.91 (d, J=6.2 Hz, 3H), 0.94 (d, J=6.4 Hz, 3H), 0.82–1.14 (m, 2H), 1.25–1.71 (m, 5H), 1.92–2.03 (m, 1H), 2.34 (sext, J_1=7.4 Hz, J_2=2.8 Hz, 1H), 2.80–2.95 (m, 2H), 3.40 (td, J_{aa}=10.4 Hz, J_{ae}=4.2 Hz, 1H), 7.10–7.36 (m, 5H). ^{13}C NMR (50 MHz) δ: 137.24, 128.81, 125.61, 71.04, 47.58, 45.01, 39.36, 34.19, 31.52, 30.99, 23.18, 22.09, 13.88. MS (CI): 265 (M^++1) 60%, 247 [(M^++1)−H_2O] 100%.

3.2.10. (−)-(1*R*,2*S*,5*R*,1′*R*)-5-Methyl-2-(1-methyl-2-phenylthio-ethyl)-cyclohexanol 19b. The title compound was also isolated by repeated chromatography of the residue after isolation of the isomer **19a** using toluene/ethyl acetate 95:5 as an eluent. Stereoisomer **19b** was isolated as a viscous colorless oil (9.8 mg, 3.7% yield), $[\alpha]_D^{22}$=−44.0 (c=1, $CHCl_3$). Anal. calcd $C_{16}H_{24}OS$: C, 72.67; H, 9.15; S, 12.13. Found: C, 72.33; H, 9.15; S, 12.22. IR (neat, cm^{-1}): 3364, 2000–1600, 1583, 1476, 1449, 1376, 1304, 1258, 1223, 1170, 1090, 1022, 969, 922, 891, 847, 740, 694. ^1H NMR (200 MHz) δ: 0.90 (d, J=6.6 Hz, 3H), 1.07 (d, J=6.9 Hz, 3H), 0.81–1.14 (m, 3H), 1.26–1.45 (m, 2H), 1.57–1.70 (m, 2H), 1.87–1.98 (m, 1H), 2.05–2.25 (m, 1H), 2.70 (dd, J_{gem}=12.6 Hz, J_{vic}=9.1 Hz, 1H), 3.15 (dd, J_{gem}=12.6 Hz, J_{vic}=4.9 Hz, 1H), 3.50 (td, J_{aa}=10.4 Hz, J_{ae}=4.2 Hz, 1H), 7.10–7.38 (m, 5H). ^{13}C NMR (50 MHz) δ: 137.29, 128.80, 128.77, 125.60, 71.05, 49.19, 45.05, 37.56, 34.42, 33.02, 31.46, 25.77, 22.02, 17.09.

3.2.11. (−)-(1*R*,3*R*,4*S*,8*S*)-Menthane-3,9-diol (31a). The title compound was prepared from **19a**,[19,20] white crystals, mp 90°C (lit. 90°C),[18] $[\alpha]_D^{22}$=−48.6 (c=1, $CHCl_3$). IR (KBr, cm^{-1}): 3256, 3223, 1487 1455, 1413, 1375, 1345, 1324, 1276, 1234, 1168, 1107, 1081, 1050, 1017, 1000, 954, 918, 883, 845, 744. ^1H NMR (200 MHz) δ: 0.85 (d, J=7.1 Hz, 3H), 0.91 (d, J=6.6 Hz, 3H), 0.71–1.12 (m, 3H), 1.25–1.55 (m, 2H), 1.58–1.68 (m, 2H), 1.93–2.11 (m, 2H), 5.39 (s, broad, 2H), 3.43 (td, J_{aa}=10.6 Hz, J_{ae}=4.2 Hz, 1H), 3.48 (dd, J_{gem}=10.6 Hz, J_{vic}=7.6 Hz, 1H), 3.58 (dd, J_{gem}=10.6 Hz, J_{vic}=5.6 Hz, 1H). ^{13}C NMR (50 MHz) δ: 71.59, 66.53, 45.50, 45.04, 35.52, 34.28, 31.48, 25.16, 22.12, 12.47.

Spectral evidence and mp of diastereoizomer **31a** independently prepared from (−)-isopulegol are identical with the same isomer prepared from **19a** and has $[\alpha]_D^{22}$=−44.0 (c=1, $CHCl_3$).

3.2.12. (−)-(1*R*,3*R*,4*S*,8*R*)-Menthane-3,9-diol (31b). The title compound was prepared from **19b**, white crystals, mp 107°C (lit. 107°C),[18] $[\alpha]_D^{22}$=−16.2 (c=1, $CHCl_3$). IR (KBr, cm^{-1}): 3251, 1487, 1455, 1372, 1337, 1309, 1272, 1218, 1171, 1150, 1103, 1043, 1018, 993, 951, 846, 698. ^1H NMR (200 MHz) δ: 0.92 (d, J=6.9 Hz, 3H), 0.96 (d, J=7.6 Hz, 3H), 0.77–1.05 (m, 2H), 1.12–1.48 (m, 3H), 1.50–1.69 (m, 2H), 1.76–2.03 (m, 2H), 3.28 (s, broad, 2H), 3.45 (td J_{aa}=10.4 Hz, J_{ae}=4.2 Hz, 1H), 3.58 (dd, J_{gem}=10.6 Hz,

J_{vic}=3.5 Hz, 1H), 3.66 (dd, J_{gem}=10.6 Hz, J_{vic}=5.3 Hz, 1H). ^{13}C NMR (50 MHz) δ: 70.06, 67.07, 48.49, 44.50, 38.56, 34.54, 31.39, 29.49, 22.01, 11.85.

Stereoisomer **31b** independently prepared from (−)-isopulegol has identical spectral evidence and mp as the same isomer prepared from **19b** and $[\alpha]_D^{22}=-15.6$ (c=1, $CHCl_3$).

3.2.13. *t*-3,*t*-5-Dimethyl-*c*-3-phenylthiomethyl-*r*-cyclohexanol (18). The title compound was isolated as a colorless oil in 62% yield in the photolysis of *trans*-3,3,5-trimethylcyclohexyl benzenesulfenate in the presence of hexabutylditin. Anal. calcd $C_{15}H_{22}OS$: C, 71.95; H, 8.86; S, 12.81. Found: C, 71.72; H, 8.73; S, 12.69. IR (neat, cm^{-1}): 3410, 2000–1600, 1584, 1481, 1456, 1439, 1377, 1366, 1337, 1290, 1262, 1218, 1174, 1152, 1091, 1043, 1026, 1013, 949, 909, 809, 756, 737, 691. ^{1}H NMR (200 MHz) δ: 0.85 (d, J=6.6 Hz, 3H), 1.00 (s, 3H), 0.82–2.02 (m, 8H), 3.31 (AB q, $\Delta\delta_{AB}$=0.28, J=11.8 Hz, 2H), 4.15 (quint, J=3.2 Hz, 1H), 7.09–7.29 (m, 3H), 7.34–7.40 (m, 2H). ^{13}C NMR (50 MHz) δ: 137.99, 129.31, 128.77, 125.60, 67.69, 46.71, 44.95, 41.57, 41.09, 34.76, 30.48, 22.31, 22.24. MS (CI): 251 (M^++1) 100%, [M^++1)−H_2O] 50% (exact mass: 250.14; mol. wt: 250.40).

3.2.14. 3β-Acetoxy-20β-hydroxy-18-phenylthio-5-pregnene (20). The title compound was obtained in 40% yield by photolysis of 3β-acetoxy-5-pregnen-20β-yl benzenesulfenate according to the general procedure. White crystalline compound, mp 149°C. IR (KBr, cm^{-1}): 3464, 2000–1600, 1730, 1582, 1441, 1370, 1247, 1135, 1032, 943, 879, 735. ^{1}H NMR (200 MHz) δ: 0.92 (s, 3H), 1.14 (d, J=6.2 Hz, 3H), 0.88–1.95 (m, 18H), 2.01 (s, 3H), 2.25–2.36 (m, 2H), 2.93 (AB q, $\Delta\delta_{AB}$=0.46, J=12.2 Hz, 2H), 3.76–3.94 (m, 1H), 4.52–4.68 (m, 1H), 5.36 (d, J=4.8 Hz, 1H), 7.21–7.42 (m, 5H). ^{13}C NMR (50 MHz) δ: 170, 36, 139.69, 136.88, 129.94, 128.94, 126.46, 121.99, 73.67, 69.47, 58.65, 57.16, 49.60, 46.13, 37.91, 36.72, 36.38, 36.08, 34.05, 31.83, 31.57, 27.51, 25.48, 23.92, 22.15, 21.24, 19.13. HRMS calcd for $C_{29}H_{40}O_3S$ (M^+): 468.2703. Found: 468.2698.

3.2.15. 3β-Acetoxy-20α-hydroxy-18-phenylthio-5-pregnene (21). The title compound was obtained as a white crystalline compound in 40% yield by photolysis of 3β-acetoxy-5-pregnen-20α-yl benzenesulfenate as described above. IR (KBr, cm^{-1}): 3451, 2000–1600, 1731, 1582, 1439, 1370, 1246, 1031, 955, 874, 739. ^{1}H NMR (200 MHz) δ: 0.99 (s, 3H), 1.25 (d, J=6.2 Hz, 3H), 0.95–1.98 (m, 18H), 2.03 (s, 3H), 2.26–2.37 (m, 2H), 2.32 (AB q, $\Delta\delta_{AB}$=0.12, J=11.4 Hz, 2H), 4.16–4.27 (m, 1H), 4.54–4.67 (m, 1H), 5.38 (d, J=4.4 Hz, 1H), 7.19–7.38 (m, 5H). ^{13}C NMR (50 MHz) δ: 170.55, 139.79, 136.41, 129.74, 129.06, 126.49, 122.22, 73.80, 65.28, 57.88, 57.58, 49.97, 44.87, 38.00, 36.90, 36.63, 34.63, 34.21, 31.68, 27.64, 23.43, 21.35, 20.56, 19.23. HRMS calcd for $C_{29}H_{40}O_3S$ (M^+): 468.2703. Found: 468.2698.

3.2.16. *exo*- and *endo*-6-Phenylthio-*N*-carbethoxy nortropine (22). A solution of *N*-carbethoxy nortropine-3α-benzenesulfenate (1.5 g, 4.88 mmol) and hexabutylditin (0.44 g, 0.76 mmol) in benzene was irradiated for 1.5 h and the title compound was isolated (2.7 g, 45%) yield) as a white crystalline compound, mp 119°C. Anal. calcd $C_{16}H_{21}NO_3S$: C, 62.54; H, 6.84; N, 4.56. Found: C, 62.51; H, 6.71; N, 4.44. IR (KBr, cm^{-1}): 3413, 2000–1600, 1661, 1483, 1431, 1384, 1330, 1162, 1114, 1097, 1046, 1011. ^{1}H NMR (200 MHz) δ: 1.21–1.30 (m, 3H), 1.69–2.20 (m, 6H), 2.69–2.84 (m, 1H), 4.10–4.40 (m, 5H), 7.18–7.36 (m, 5H). ^{13}C NMR (50 MHz) δ: 154.59, 154.25, 136.86, 136.65, 129.92, 129.82, 128.90, 126.24, 64.54, 61.05, 59.55, 59.36, 53.02, 52.76, 47.88, 47.14, 38.29, 37.99, 37.69, 37.63, 36.92, 36.15. MS (CI): 308 (M^++1) 100%.

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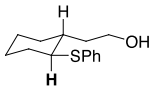
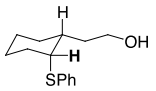
16. In the ^{1}H NMR spectrum of the mixture of isomers **15** two signals were obtained for hydrogens next to the phenylthio group, signals at δ=2.84 ppm belong to the *trans*-isomer **15a** and at δ=3.50 ppm are from the *cis*-isomer **15b** and they possess different coupling constants. This is in agreement with described results. Eliel, E.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994, pp 712.

d_H = 2.84
J_{aa} = 10.1 Hz
J_{ae} = 3.6 Hz



15a 1 : 0.86 **15b**



d_H = 3.50
J_{ee} = 4.4 Hz
J_{ea} = 3.4 Hz

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