LEWIS-ACID- OR HIGH-PRESSURE-INITIATED REGIO- AND STEREOSELECTIVE FUNCTIONALIZATION OF ISOPRENE UTILIZING PHENYLSULFINYL CHLORIDE*

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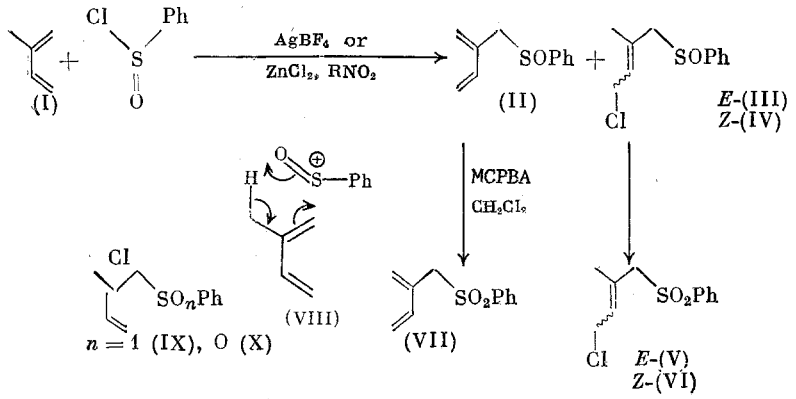
Electrophilic addition of arylsulfenyl chlorides is used as a general method for the functionalization of unsaturated compounds [2]; the feasibility of utilizing arylsulfinyl chlorides ArSOCl [3-5] in an analogous Ad_E reaction has not been adequately investigated. It is known, however, that the latter reagents react with alkenes only in the presence of Lewis acids. For example, styrene and its derivatives react with ArSOCl upon treatment with $ZnCl_2$ to generate the corresponding β-chlorosulfoxides [3]; olefins react with ArSOCl in the presence of $EtAlCl_2$ to give products resulting from ene reactions [4], whereas in the presence of $TiCl_4$ treatment of ArSOCl with trimethylsiloxyalkenes leads to the formation of α-ketosulfides [5]. There have been no reports concerning reaction possibilities involving ArSOCl and 1,3-dienes.

As part of our search for efficient methods for the functionalization of isoprene (I), we have studied and report herein the reaction of (I) with PhSOCL under various conditions. It has been found that reaction of (I) with PhSOCL in the absence of catalysis proceeds very slowly (at 25°C the conversion of (I) is 20-30% after 7-10 days) and gives a complex mixture of products. Attempts to force the reaction by heating to 100°C were unsuccessful due to the thermal lability of PhSOCl and the resulting products. In contrast, in the presence of Lewis acids the reaction of (I) with PhSOCl occurs rapidly even at low temperatures. When the reaction was carried out at −70°C in n-$PrNO_2$ in the presence of $ZnCl_2$, 2-phenylsulfinylmethylbuta-1,3-diene (II) was obtained in ~90% yield. At a higher temprature (−20°C, $MeNO_2$), a mixture of chlorosulfoxides (III) and (IV) was formed in addition to (II), in the ratio (II):(III):(IV) = ca. 6:2:1 at a total yield of ca. 90% (based on PMR spectral data at 250 MHz). Compounds (II) and (III) were isolated chromatographically in yields of ca. 60 and 20%, respectively, whereas chloride (IV) underwent decomposition upon chromatography on SiO_2. Other Lewis-acid catalysts ($Et_2O{\cdot}BF_3$, $SnCl_4$, $TiCl_4$, $SbCl_5$) led to the formation of significant amounts of side products. Exclusive formation of (II), in 73% isolated yield, was observed upon reaction of (I) with PhSOCl in the presence of $AgBF_4$ ($MeNO_2$, −25°C).

The structure of diene (II), whose synthesis has been previously communicated [6], as well as the structure of the previously unknown E-chlorosulfoxide (III), were established by physicochemical methods and elemental analysis, and on the basis of their conversion



*For preliminary communication, see [1].

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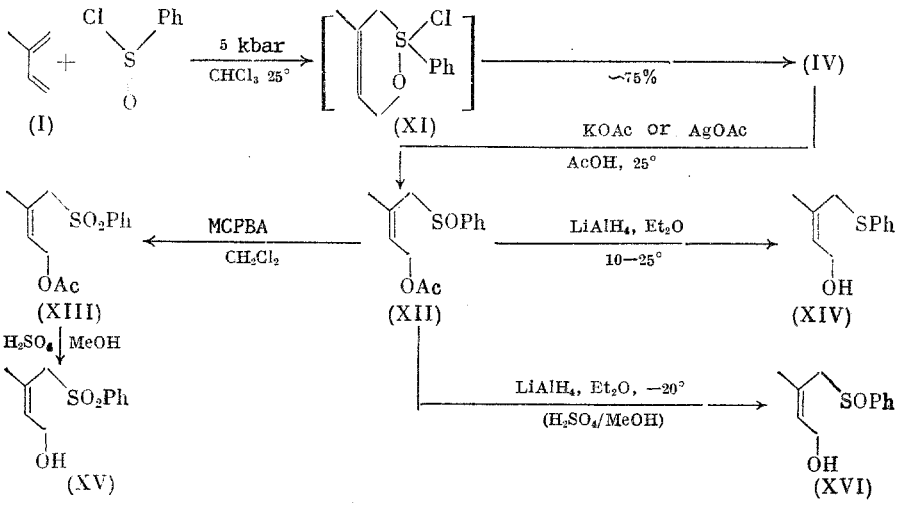
to the known sulfones (V) and (VII) [7, 8] upon treatment with m-chloroperbenzoic acid (MCPBA). The data verifying the structure of the Z-chlorosulfoxide (IV) is discussed below.

The formation of compound (II) can be explained in terms of an ene reaction involving phenylsulfoxonium ion in a transition state such as that shown in (VIII). The appearance of E- and Z-sulfoxides (III) and (IV) can be attributed apparently to allylic rearrangement of intermediate (IX), which is similar to sulfide (X) which has been identified in the first stage of addition of PhSCl to isoprene [9].

Taking into account the reactivity of PhSOCl with respect to an ene reaction with isoprene, it remained of interest to determine the feasibility of utilizing the multiple bonds in these molecules in a heterodiene synthesis. It is known that [4 + 2] cycloaddition reactions are steeply accelerated at high pressures [10], and this method was therefore utilized to meet the desired objective. It was found that maintaining a mixture of (I) and PhSOCl in a 3:1 ratio in $CHCl_3$ at 5 kbar and 25°C for 3 days gave the Z-chlorosulfoxide (IV) in ca. 75% yield, without contamination due to the E-isomer (III) or diene (II). The structure of (IV) was established based on its PMR spectrum, which exhibited signals due to the CH_2SO protons (AB pattern, δ 3.59 ppm) and the CH_2Cl protons (AB portion of an ABX spectrum, δ 3.87 ppm), as well as by comparison of the chemical shifts of the carbon atoms in these groups in the ^{13}C-NMR spectra of isomers (IV) and (III), namely 60.6 and 39.8 and 67.7 and 39.5 ppm, respectively. In addition, oxidation of (IV) with MCPBA gave the known sulfone (VI) [8]. The ^{13}C-NMR spectra of (V) and (VI) exhibited a relative shift of the signals due to the CH_2S protons toward higher field ($\Delta\delta$ = ca. 7 ppm) for the Z-isomer, just as was observed in the case of the sulfoxide pair E-(III) and Z-(IV).



The formation of Z-sulfoxide (IV) at high pressure can be rationalized in terms of initial [4 + 2] cycloaddition of PhSOCl to (I). Subsequent ionization of the S—Cl bond in the postulated sulfurance intermediate (XI), followed by nucleophilic cleavage of the C—O in the resulting sulfoxonium ion, would be expected to give (IV) with retention of the cis-configuration of the C=C bond in (XI).

Acetolysis of chloride gave the acetate (XII). Reduction of the latter with $LiAlH_4$ in Et_2O at 20°C generated the hydroxysulfoxide (XVI) in ca. 70% yield. Hydroxysulfide (XIV) was also isolated in ca. 10% yield under these conditions, and it constituted the main reaction product when the reaction was carried out at 10-25°C. Sulfoxide (XVI) was also formed upon hydrolysis of (XII) with H_2SO_4 in MeOH. Oxidation of (XII) with MCPBA in CH_2Cl_2 gave sulfone (XIII), which could be hydrolyzed to the hydroxysulfone (XV). The PMR spectrum of (XV) was identical to that described previously [8].

The structures of the previously unknown Z-olefins (XII) and (XIV), as well as of compounds (XIII), (XV), and (XVI), which have been partially described earlier [8, 11, 12], were established by a combination of physicochemical methods and elemental analyses. The

chemical shift values (δ = ca. 24 ppm) for the CH_3 groups in the ^{13}C-NMR spectra of these substances, as well as in the chlorides (IV) and (VI), are characteristic of Z-trisubstituted olefins, and are larger than the measured values for the E-isomers by $\Delta\delta$ = ca. 7 ppm. The literature does not contain many examples of the stereospecific synthesis of 1,4-bifunctional derivatives of isoprene containing a Z-trisubstituted C=C bond [13, 14]. Similar compounds have been utilized as synthons for the construction of regular chain isoprenoids. Thus, for example, a hydroxysulfonamide related to compounds (XIV)-(XVI) has been used as the basis for a stepwise synthesis of polyprenoids [15]. With respect to the dienyl sulfoxide (II), it could probably be used for the synthesis of linear and cyclic terpenoids.

It should be emphasized that, in all of the Ad_E reactions (I) involving ArSCl which have been reported previously, mixtures of regio- and stereoisomeric adducts were obtained [9]. The high regioselectivity which was observed for electrophilic attack at the C^1 site is characteristic of cationic reagents of the type ArS^+X^-, although the 1,4-adducts formed in this manner usually consist of mixtures of E/Z-isomers [16]. Oxidative addition of thiophenol to (I) was also nonselective [11]. For this reason, the high degree of regioselectivity observed for the reaction of PhSOCl with isoprene (I) under both sets of reaction conditions is especially interesting. The results presented here can be considered to be generally applicable to other 1,3-dienes as well.

EXPERIMENTAL

Melting points wre taken on a Kofler block. IR spectra (in $CHCl_3$) were obtained on a UR-20 spectrophotometer, PMR spectra on Tesla BS-497 (100 MHz) and Bruker WM-250 spectrometers, and ^{13}C-NMR spectra were recorded at 62.89 MHz on a Bruker WM-250 spectrometer, using the $CDCl_3$ solutions relative to TMS. Mass spectra were taken on a Varian MAT CH-6 instrument at 70 eV. R_f values were measured on Silufol bound SiO_2 plates.

2-Phenylsulfinylmethylbuta-1,3-diene (II) and 1-Chloro-4-phenylsulfinyl-3-methylbut-2E-ene (III). A solution of 0.2 g (2.94 mmole) of (I) in 5 ml $MeNO_2$ (under Ar) was stirred at −25°C and 0.5 ml of a 2M solution of $AgBF_4$ (1 mmole) in dichloroethane was added, followed by a solution of 0.16 g (1 mmole) of PhSOCl [17] in 2 ml $MeNO_2$. The mixture was stirred for 10 min at −25°C and worked up with 50 ml Et_2O and 5 ml H_2O. The aqueous layer was neutralized with $NaHCO_3$ and extracted with Et_2O. The combined organic extracts were washed with water, dried over $MgSO_4$, and evaporated, and the residue (0.27 g) was chromatographed on 15 g SiO_2 using 2:3 ether–hexane. Yield, 0.14 g (73%) of (II) as a colorless oil, bp 100-103°C (0.05 mm Hg) (dec.), n_D^{20} 1.5890. IR spectrum (ν, cm^{-1}): 700, 915, 990, 1040, 1070, 1085, 1135, 1250, 1305, 1395, 1445, 1480, 1590, 1630, 1670, 2930, 3010, 3070, 3100. UV spectrum (λ_{max}, nm): 213 (ε 10,000), 232 (ε 7500) (EtOH). PMR spectrum (δ, ppm): 3.69 d of d (2H, CH_2S, J_{AB} = 12 Hz), 4.9-5.5 m (4H, H_2C=C), 6.3 m (1H, HC=C), 7.5 m (5H, C_6H_5). Found: C 68.26; H 6.38; S 16.77%. M^+ 192. $C_{11}H_{12}OS$. Calc.: C 68.74; H 6.40; S 16.34%; mol. wt. 192.3.

A stirred solution of 0.2 g (2.94 mmole) of (I) in 5 ml n-$PrNO_2$ at −70°C (under Ar) was treated with 0.18 g (1.32 mmole) $ZnCl_2$, followed by a solution of 0.21 g (1.31 mmole) PhSOCl in 2 ml n-$PrNO_2$. The mixture was heated to 25°C and worked up as described above. The oily product (0.25 g) was chromatographed on 15 g SiO_2. Gradient elution from hexane to ether (to 50% of the latter) gave 0.22 g (87%) of (II) and 30 mg (10%) of (III) as colorless crystals, mp 65-66°C (ether–hexane). IR spectrum (ν, cm^{-1}): 665, 680, 860, 870, 1025, 1045, 1090, 1260, 1385, 1450, 1475, 1580, 1660, 2875, 3005, 3060. PMR spectrum (δ, ppm): 1.80 br. s (3H, CH_3), 3.54 s (2H, CH_2S), 4.09 d (2H, CH_2Cl, J = 8 Hz), 5.52 br. t (1H, HC=C, J = 8 Hz). 7.6 m (5H, C_6H_5). ^{13}C-NMR spectrum (δ, ppm): 17.1 (CH_3), 39.5 (C^1), 67.7 (C^4), 128.5 (C^2), 131.3 (C^3), 124.1, 129.1, 131.1, 143.5 (C_6H_5). Found: C 57.49; H 5.82; Cl 15.26; S 13.80%, M^+ 228. $C_{11}H_{13}ClOS$. Calc.: C 57.76; H 5.73; Cl 15.50; S 14.02%; mol. wt. 228.7.

2-Phenylsulfonylmethylbuta-1,3-diene (VII). A solution of 0.41 g (2.13 mmole) of (II) and 0.4 g (2.32 mmole) of MCPBA in 10 ml CH_2Cl_2 was stirred for 1.5 h at −40°C, diluted with 20 ml hexane, and the precipitate was filtered and washed with cold CH_2Cl_2–hexane (1:3). The combined filtrates were evaporated under vacuum and the residue was chromatographed on 30 g SiO_2. Elution with ether–hexane (1:4) gave 0.36 g (81%) of (VII), mp 65-65.5°C (ether–hexane) (cf. [8], mp 52-53°C). PMR spectrum (δ, ppm): 4.00 s (2H, CH_2S), 5.0-5.4 m (4H, H_2C=C), 6.3 m (1H, HC=C), 7.5-7.9 m (5H, C_6H_5). Found: 63.07; H 5.67; S 15.37%. M^+ 208. $C_{11}H_{12}O_2S$. Calc.: C 63.43; H 5.81; S 15.39%; mol. wt. 208.3.

1-Chloro-4-phenylsulfonyl-3-methylbut-2E-ene (V). As described above for (VII), 0.1 g (0.44 mmole) (III) and 0.1 g (0.58 mmole) MCPBA in 3 ml CH_2Cl_2 gave, after chromatography, 80 mg (74%) of (V), mp 72-72.5°C (ether–hexane) (cf. [7]). PMR spectrum (δ, ppm): 1.89 br.s (3H, CH_3), 3.78 s (2H, CH_2S), 3.97 d (2H, CH_2Cl, J = 8.5 Hz), 5.31 br. t (1H, HC=C, J = 8.5 Hz), 7.5-7.9 m (5H, C_6H_5). ^{13}C-NMR spectrum (δ, ppm): 16.9 (CH_3), 39.3 (C^1), 65.6 (C^4), 129.8 (C^2), 130.5 (C^3), 128.6, 129.1, 133.8, 138.8 (C_6H_5).

1-Chloro-4-phenylsulfinyl-3-methylbut-2Z-ene (IV). A solution of 1.39 g (8.6 mmole) PhSOCl and 1.02 g (15.0 mmole) (I) in 20 ml $CHCl_3$ was maintained for 4 h in a teflon ampul at 25°C and 5 kbar pressure, and was then diluted with 70 ml ether, neutralized with $NaHCO_3$, washed with water, dried with $MgSO_4$, and evaporated under vacuum; the residue was also evacuated completely (1 mm Hg) for 1 h at 40°C. Yield 1.7 g (86%) of (IV), as an unstable light-yellow oil, R_f 0.52 (ether–hexane, 4:1). IR spectrum (ν, cm^{-1}): 890, 910, 950, 990, 1025, 1060, 1085, 1090, 1170, 1185, 1230, 1255, 1380, 1440, 1450, 1480, 1600, 1660, 2860, 2950, 2980, 3010, 3085. PMR spectrum (δ, ppm): 1.76 br.s (3H, CH_3), 3.59 d of d (2H, CH_2S, J_{AB} = 12.5 Hz), 3.9 m (2H, CH_2Cl), 5.77 br. t (1H, HC=C, J = 8.5 Hz), 7.5-7.7 m (5H, C_6H_5). ^{13}C-NMR spectrum (δ, ppm): 24.2 (CH_3), 39.8 (C^1), 60.6 (C^4), 128.8 (C^2), 131.6 (C^3), 123.9, 129.1, 131.2, 143.4 (C_6H_5). Found: M^+ 228. Calc. for $C_{11}H_{13}ClOS$: mol. wt. 228.7.

1-Chloro-4-phenylsulfonyl-3-methylbut-2Z-ene (VI). As described above for (VII), 0.4 g (1.75 mmole) (IV) and 0.34 g (1.97 mmole) MCPBA in 10 ml CH_2Cl_2 gave, after chromatography, 0.3 g (70%) of (VI), mp 88-89°C (ether–hexane) (cf. [8], mp 78-80°C). IR spectrum (ν, cm^{-1}): 670, 685, 865, 880, 1025, 1075, 1080, 1130, 1150, 1170, 1260,1295, 1310, 1330, 1380, 1415, 1450, 1470, 1580, 1600, 1660, 2930, 2930, 2970, 3030, 3060. PMR spectrum (δ, pm): 1.89 br.s (3H, CH_3), 3.78 br.d (2H, CH_2Cl, J = 8.5 Hz), 3.89 s (2H, CH_2S), 5.78 br. t (1H, HC=C, J = 8.5 Hz), 7.5-8.0 m (5H, C_6H_5). ^{13}C-NMR spectrum (δ, ppm): 24.2 (CH_3), 39.7 (C^1), 59.1 (C^4), 128.3, 129.3, 130.0, 134.0, 138.8 (C^2, C^3, C_6H_5). Found: C 53.84; H 5.45; Cl 14.41; S 13.02%. $C_{11}H_{13}SO_2Cl$. Calc.: C 53.59; H 5.35; Cl 14.48; S 13.10%.

1-Phenylsulfinyl-4-acetoxy-2-methylbut-2Z-ene (XII). A suspension of 0.7 g (3.06 mmole) of (IV) and 0.52 g (3.12 mmole) AgOAc in 10 ml AcOH was stirred for 10 min at 25°C, and the precipitate was filtered, washed with Et_2O; the combined filtrate was evaporated under vacuum and the residue (0.72 g) was chromatographed on 30 g SiO_2. Gradient elution from hexane to ether (to 50% of the latter) gave 0.4 g (52%) of (XII) as a colorless oil, R_f 0.32 (ether–hexane, 4:1). IR spectrum (ν, cm^{-1}): 960, 980, 1000, 1025, 1050, 1090, 1250, 1280, 1360, 1380, 1450, 1480, 1580, 1665, 1730, 2920, 3000, 3060. PMR spectrum (δ, ppm): 1.76 br.s (3H, CH_3–C^2), 1.97 s (3H, CH_3), 3.60 d of d (2H, CH_2S, J_{AB} = 12.5 Hz), 4.3 m (2H, CH_2O), 5.64 br. t (1H, HC=C, J = 7.5 Hz), 7.5 m (5H, C_6H_5). ^{13}C-NMR spectrum (δ, ppm): 20.7 (CH_3), 24.5 (CH_3–C^2), 60.2 (C^1), 61.0 (C^4), 127.1 (C^3), 130.7 (C^2), 170.5 (C=O), 124.1, 129.1, 131.2, 143.7 (C_6H_5). Found: C 61.70; H 6.30; S 12.74%. M^+252. $C_{13}H_{16}O_3S$. Calc.: C 61.88; H 6.39; S 12.71%; mol. wt. 252.3

A solution of 0.28 g (1.22 mmole) of (IV) and 0.25 g (2.55 mmole) KOAc in 5 ml AcOH was stirred for 15 h, then diluted with 15 ml of a 1:2 ether–hexane mixture. The precipitate was filtered and washed with ether, and the combined filtrate was evaporated under vacuum; the oily residue was chromatographed under the conditions described above. Yield, 0.17 g (55%) of (XII), identical (by TLC and PMR) to the same prepared above.

1-Phenylsulfonyl-4-acetoxy-2-methylbut-2Z-ene (XIII). As described above for (VII), 0.18 g (0.71 mmole) (XII) and 0.18 g (1.04 mmole) MCPBA in 5 ml CH_2Cl_2 gave 0.25 g of product, which was chromatographed on 10 g SiO_2. Gradient elution with hexane to ether (to 50% of the latter) gave 0.16 g (84%) of (XIII) as a colorless oil, R_f 0.29 (ether–hexane, 2:1). IR spectrum (ν, cm^{-1}): 650, 685, 840, 880, 915, 985, 1030, 1090, 1140, 1160, 1225, 1270, 1295, 1310, 1320, 1370, 1380, 1415, 1450, 1470, 1590, 1620, 1675, 1780, 2925, 2960, 2980, 3020, 3030, 3060. PMR spectrum (δ, ppm): 1.83 br.s (3H, CH_3–C^2), 1.94 s (3H, CH_3), 3.91 s (2H, CH_2S), 4.16 br.d (2H, CH_2O, J = 7.5 Hz), 5.60 br. t (1H, HC=C, J = 7.5 Hz), 7.5-7.9 m (5H, C_6H_5). ^{13}C-NMR spectrum (δ, ppm): 20.4 (CH_3), 24.2 (CH_3–C^2), 59.1 (C^1), 60.0 (C^4), 170.2 (C=O), 128.0, 128.1, 128.4, 129.0, 133.6, 138.6 (C^2, C^3, C_6H_5). Found: C 58.37; H 6.24; S 11.56%. $C_{13}H_{16}O_4S$. Calc.: C 58.19; H 6.01; S 11.95%.

1-Phenylmercapto-2-methylbut-2Z-en-4-ol (XIV). A solution of 4.8 g (19 mmole) (XII) in 50 ml Et_2O (under Ar) was stirred at 10°C and 1.8 g (47.4 mmole) $LiAlH_4$ was added over 1 h. The mixture was stirred an additional 30 min at 25°C, and then decomposed with 10 g of a mixture of $Na_2SO_4 \cdot 10H_2O$ and cellite (1:1 by volume). The precipitate was removed by filtration,

washed with Et_2O, and the combined filtrate was evaporated to give an oil product, which was subjected to chromatography on 100 g SiO_2. Gradient elution with hexane to ether (to 50% of the latter) gave 2.73 g (74%) of (XIV) as a colorless liquid, bp 96-98°C (0.07 mm Hg), n_D^{20} 1.5840. IR spectrum (ν, cm^{-1}): 690, 900, 950, 995, 1030, 1070, 1090, 1150, 1180, 1240, 1300, 1350, 1380, 1440, 1480, 1585, 1660, 2880, 2920, 2940, 2975, 3010, 3060, 3080, 3450, 3570, 3610. PMR spectrum (δ, ppm): 1.88 br. s (3H, CH_3), 3.50 s (2H, CH_2S), 3.78 br. z (2H, CH_2O, J = 7 Hz), 5.48 br. t (1H, HC=C, J = 7 Hz), 7.2-7.5 m (5H, C_6H_5). ^{13}C-NMR spectrum (δ, ppm): 22.8 (CH_3), 37.0 (C^1), 58.8 (C^4), 128.0 (C^3), 134.8 (C^2), 127.4, 128.9, 132.3, 135.7 (C_6H_5). Found: C 68.15; H 7.27; S 16.25%. M^+ 194. $C_{11}H_{14}OS$. Calc.: C 68.00; H 7.26%; S 16.25%; mol. wt. 194.3.

1-Phenylsulfinyl-2-methylbut-2Z-en-4-ol (XVI). A stirred solution of 1.9 g (7.53 mmole) (XII) in 15 ml Et_2O (under Ar) at −20°C was treated with 0.38 g (10 mmole) of $LiAlH_4$ over a 30-min period. The mixture was maintained at −20°C for 1 h, and then decomposed with 5 g of a mixture of $Na_2SO_4 \cdot 10H_2O$ and cellite, and worked up as described above. Yield, 1.95 g of product, which was chromatographed on 50 g SiO_2. Gradient elution with hexane to ether gave 1.1 g (70%) of (XVI) and 0.18 g (12%) (XIV), which was identical (by TLC and PMR) to the sample prepared as above.

Hydroxysulfoxide (XVI) gave colorless crystals, mp 37-38°C (ether–hexane). PMR spectrum (δ, ppm): 1.69 br. s (3H, CH_3), 3.59 d of d (2H, CH_2S, J_{AB} = 14 Hz), 3.9 m (2H, CH_2O), 5.95 br. t (1H, HC=C, J = 6 Hz), 7.6 m (5H, C_6H_5). ^{13}C-NMR spectrum (δ, ppm): 24.0 (CH_3), 57.7 (C^4), 60.7 (C^1), 127.6 (C^3), 133.8 (C^2), 123.9, 129.1, 131.2, 142.9 (C_6H_5).

A solution of 0.58 g (2.3 mmole) of (XI) and 0.1 ml 50% H_2SO_4 in 5 ml MeOH was treated at 25°C for 15 h, diluted with 50 ml Et_2O, and neutralized with $NaHCO_3$; the mixture was then washed with water, dried over $MgSO_4$, and the residue remaining (0.55 g) after solvent evaporation under vacuum was chromatographed on 20 g SiO_2. Gradient elution with hexane–ether gave 0.4 g (83%) of (XVI) which was identical (by TLC) and PMR) with a sample prepared above.

1-Phenylsulfonyl-2-methyl-2Z-en-4-ol (XV). As described above for (XVI), reaction of 0.5 g (1.86 mmole) of (XIII) and 0.3 ml 50% H_2SO_4 in 10 ml MeOH gave 0.54 g of an oily substance, which was chromatographed on 20 g SiO_2. Gradient elution with hexane–ether gave 0.37 g (88%) of (XV) as colorless crystals, mp 55.5-56.6°C (ether–benzene). IR spectrum (ν, cm^{-1}): 890, 950, 1005, 1090, 1150, 1240, 1310, 1410, 1450, 1590, 1665, 2890, 2940, 2980, 3015, 3035, 3070, 3520, 3610. PMR spectrum (δ, ppm): 1.73 br. s (3H, CH_3), 3.81 br. d (2H, CH_3O, J = 7.5 Hz), 3.86 s (2H, CH_2S), 5.79 br. t (1H, HC=C, J = 7.5 Hz), 7.5-7.8 m (5H, C_6H_5). ^{13}C-NMR spectrum (δ, ppm): 24.7 (CH_3), 58.7 (C^4), 59.2 (C^1), 125.9 (C^3), 134.0 (C^2), 128.2, 129.3, 133.8, 138.8 (C_6H_5). Found: C 58.70; H 6.04; S 14.22%. M^+ 226. $C_{11}H_{14}O_3S$. Calc.: C 58.38; H 6.23; S 14.17%; mol. wt. 226.3.

CONCLUSIONS

1. Treatment of isoprene with phenylsulfinyl chloride in the presence of Lewis acids results in a highly selective ene reaction; at high pressure the two components react regiospecifically via a heterodiene synthesis.

2. A series of 1,4-bifunctional isoprene derivatives, which may be regarded as potential synthons for the construction of linear and cyclic isoprenoids, has been prepared.

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SYNTHESIS OF PRENOLS $\omega t_2 c_2 sOH$ and $\omega t_3 c_2 sOH$ RELATED TO DOLICHOLS

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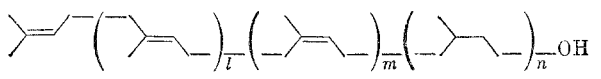
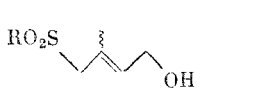
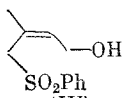
A new class of membrane-active bioregulators, belonging to the group of polyprenols (I), has been discovered [1, 2] in microorganisms and also in the cells of plants and mammals. Among these, the subgroup of dolichols (I; ℓ = 2, m = 12-18, n = 1), which are characteristic of eucariotes and control therein the biosynthesis of glycoproteins [2], are obtainable with difficulty. A search is therefore necessary for paths of synthesizing these and related compounds. Recently, a partial synthesis of a composite preparation of dolichols from the corresponding plant polyprenols (I, ℓ = 2, m = 12-18, n = 0) has been reported [3]. In the present work, racemic compounds indicated in the title were obtained (Ia; ℓ = m = 2, n = 1 and Ib; ℓ = 3, m = 2, n = 1) by a two-step C_5-homologization of a suitable prenol, and were used for the first time to obtain the hexa- and heptaprenols (I; ℓ = 2, 3, m = 3, n = 0) and also certain modified members of the same series based on Z-(II) and E-(III) C_5-synthones [4-7].



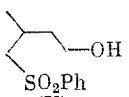
(I) $l = 2, 3$; $m \geqslant 3$; $n = 0, 1$



R = $N(CH_2)_4O$, Z-(II)
R = Ph, E-(III)



(IV)



(V)

The synthesis of the desired molecules (Ia, b) was carried by means of hydroxysulfones Z-(IV) [8] and (V) [9], of which the former was found to be substantially more available than sulfonamide (II). The condensation of a mixture of allyl bromides (VII; E/Z ≈ 3:1), freshly prepared according to [6] from geranyllinalool (VI), with a dilithium derivative of (IVa) hydroxysulfone (IV) in THF medium at −70°C, gives sulfones (VIII) and (IX) in a yield of ∼70%, with a relative content of (VIII) of up to 25% (data of column chromatography on SiO_2). Reduction of the individual Z, Z-(VIII) by Na in a NH_3–hexane–ether emulsion in the presence of dibenzo-18-crown-6 (DB18C6) [cf. 4-6], leads smoothly to sesterterpinols (X). Conversion of (X) into the intermediate bromide and its condensation with dilithium derivative (Va) of hydroxysulfone (V) gave alcohol (XII), which was further reduced by Na/NH_3 into phenol (Ia) in an overall yield of ∼4%, based on sulfone (VIII).

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