SYNTHESIS OF cis-1,4-BIFUNCTIONAL DERIVATIVES OF AN ISOPRENE δ-SULTONE*

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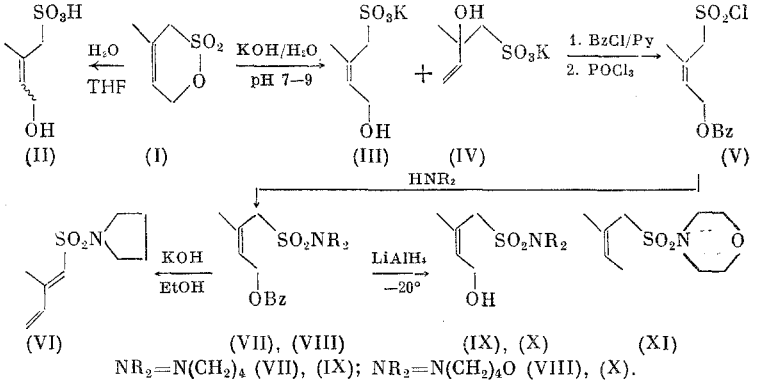
One of the modern methods for the synthesis of cyclic and linear isoprenoids is to build up the carbon chain in two stages, which include alkylation of an allyl carbanion stabilized by an adjacent S-containing functional group followed by reductive elimination of the latter [2-4]. The isoprenoid synthones used for this purpose contain a trans-trisubstituted C=C bond, since the cis-synthones needed for the synthesis of a whole series of natural substances are practically inaccessible [4]. The purpose of the present investigation was to develop a method for obtaining several cis-C_5-synthones on the basis of isoprene δ-sultone I, which we described in [5].

The possibility of utilizing derivatives of cyclosulfonate I for the two-step building up of a regular isoprenoid chain containing one cis linkage with a terminal allyl alcohol group raises the necessity of cleavage of the S–O bond in I followed by appropriate conversion of the sulfonate group, for example, into the sulfonamides and sulfones considered below. At the same time, the hydrolysis of I must rule out the possibility of the formation of a free sulfonic acid, since we have previously found [5] that the dissolution of I in aqueous THF yields a mixture of geometric isomers (II). As it was found, the controlled (pH 7-9) saponification of sultone I, which guarantees the constant neutralization of the (Z)-hydroxy acid (II) accumulated, in the 0-50°C range quantitatively yields a mixture of sulfonate III and allyl alcohol IV in an ~2:1 ratio. The ratio indicated, as well as the nature of alcohol IV, follow from the PMR spectrum of the mixture, which contains characteristic multiplets of the protons of the vinyl group (δ 5.87-6.37 ppm) and singlets of the methylene (3.07 ppm) and methyl (1.43 ppm) groups (in CD_3OD).



NR_2=N$(CH_2)_4$ (VII), (IX); NR_2=N$(CH_2)_4$O (VIII), (X).

The standard transition from the sulfonate to the sulfonyl chloride required preliminary protection of the HO group in the case of III, since the direct treatment of a mixture of III and IV with $POCl_3$ and then with pyrrolidine produces a mixture of sultone I and diene VI in an ~1:1 ratio, according to the data from the PMR spectrum. Benzoate was selected as the protective group, since the acetate of type V readily undergoes an allylic rearrangement. In addition, it was found that under the conditions adopted tertiary alcohol IV is not benzoylated and that it is destroyed in the subsequent reaction with $POCl_3$. The amount of the amine taken for binding the HCl is of decisive importance in the benzoylation step. For example, with an equivalent amount of pyridine or Et_3N as calculated for III the benzoate forms smoothly, since a small excess causes uncontrollable secondary conversions. The yield of acid chloride V with the use of $POCl_3$ at 25° is ~90% as calculated relative to III and does not exceed 2-3% in boiling $SOCl_2$.

* For the preliminary report see [1].

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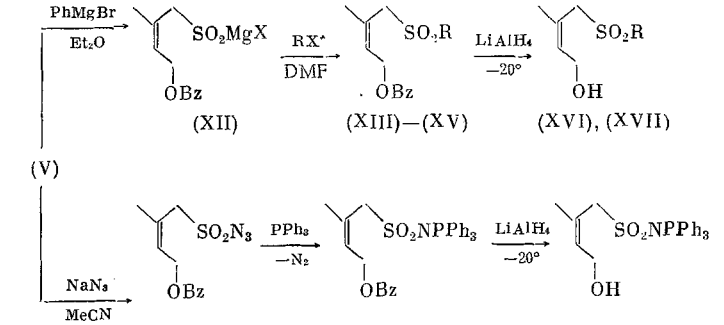
Acid chloride V was next used as the starting compound for obtaining sulfonyl derivatives IX, X, XVI, XVII, and XX. For example, its treatment with two equivalents of pyrrolidine or morpholine under mild conditions produces the corresponding sulfonamides (VII and VIII) in almost quantitative yields. The benzoate protection in the latter was stable during many hours of boiling in 10% KOH. In hydroalcoholic alkali at 80°C benzoate VII is converted after 20 h to a 30% extent into (E)-diene VI, clearly as a result of the deprotonation of the C^1 center in VII followed by 1,4 elimination of the leaving group, which has been described for related trans-1,4-bifunctional derivatives of the isoprene series [3]. The stereochemistry of VI follows from the presence in its PMR spectrum of a diagnostic [6] signal of $H-C^3$ at δ 6.38 ppm and a comparison with the spectral characteristics of structurally similar derivatives of (Z)-isoprenesulfinic acid [6]. The hydride reduction of benzoates VII and VIII at −20°C produces the corresponding allyl alcohols IX and X. An increase in the reduction temperature causes hydrogenolysis of the allyl C−O bond. Then, for example, the known [5] sulfonamide XI was obtained from VIII.



X = Br, Cl (XII); R = Me (XIII), (XVI); R = $Me_2C=CHCH_2$ (XIV), (XVII); R = $PhCH_2$ (XV).

It is known [7] that Grignard reagents react with sulfonyl chlorides to form sulfones and sulfinates. In the case of V, the reaction with PhMgBr in ether produces sulfinate XII with an almost quantitative yield. The structure of the latter was confirmed spectrally and by obtaining sulfones XIII-XV from it with high yields under the action of CH_3I, prenyl chloride, and $PhCH_2Br$, respectively, in a DMF medium at 50°C. The benzoate protection was removed with the formation of alcohols XVI and XVII precisely as in the case of the sulfonamides.

Azide XVIII was obtained with a satisfactory yield by reacting NaN_3 with V, and its treatment with triphenylphosphine produces, as in a number of acyl azides [8], ylide XIX. The structures of the latter and the product of its hydride reduction (XX) were confirmed spectrally.

The Z configuration of the key original hydroxysulfonate, III, and the allyl alcohols obtained from it without affecting the geometry of the trisubstituted double bond (IX, X, XVI, XVII, and XX) follows reliably from the data from their PMR spectra, in which the CH_3 signal is a broadened doublet with a spin−spin coupling constant of ~1.5 Hz, while this constant exceeds 2 Hz for the known related (E)-olefins [9]. In addition, the chemical shift of the easily identified quartet signal of $\underline{C}H_3C=C$ in the ^{13}C NMR spectra of alcohols X and XVI amounts to 24.6 and 24.1 ppm, respectively, and exceeds the value of the shift of the same signals in the spectra of the known related E isomers by ~ 7 ppm [10, 11]. Finally, the chemical shift of the $\underline{C}H_3$ signal in the spectrum of I has a value of 22.6 ppm.

Thus, the directed transformation of isoprene δ-sultone I has yielded a number of its cis-1,4-bifunctional derivatives, which contain a carbanion-stabilizing sulfonyl group that can be removed by reduction. Among them the allyl alcohols IX, X, XVI, and XX may be considered as potential synthones which are suitable for the cis-C_5-homologization of prenyl halides, according to the existing data for the related trans compounds [2].

EXPERIMENTAL

The IR spectra were obtained on a UR-20 instrument, and the PMR spectra were obtained on Tesla BS-497 (100 MHz) and Varian DA-60-JL spectrometers relative to TMS in $CDCl_3$ solutions. The ^{13}C NMR spectra were obtained on a Bruker WH-60 instrument in $CDCl_3$ solutions, and the mass spectra were obtained on a Varian MAT CH-6 instrument. The TLC was carried out on plates with an attached layer of SiO_2 (Silufol).

Potassium Salt of (Z)-4-Hydroxy-2-methylbut-2-ene-1-sulfonic Acid (III). A 50-ml portion of 2 N KOH was added to an intensely stirred emulsion of 14.8 g (0.1 mole) of I in 150 ml of H_2O, which was placed in the

cell of a pH-meter, at 40°C. Evaporation in a vacuum yielded 20.4 g of a powdered mixture of salts III and IV in an ~ 2:1 ratio (PMR). IR spectrum (ν, cm^{-1}): 770, 800, 925, 1050, 1080, 1190, 1225, 1300, 1420, 1645, 3400 (KBr). PMR spectrum of III (CD_3OD, δ, ppm): 2.12 d (J = 1.5 Hz, 3 H, CH_3), 3.45 s (2 H, CH_2S), 4.13 d. d (J = 1.5 and 7 Hz, 2 H, CH_2O), 5.76 br. t (J = 7 Hz, 1 H, C=CH).

(Z)-4-Benzoyloxy-2-methylbut-2-ene-1-sulfonyl Chloride (V). A suspension of 10.2 g (0.05 mole) of a mixture of salts III and IV was stirred for 5 min at 20°C in 40 ml of PhCOCl and then for another 2 h after the addition over the course of 2 min of 2 ml (35 mmole) of pyridine. The mixture was extracted with ether, and the residue was suspended in 40 ml of $POCl_3$, stirred for 30 min at 20°C, and then evaporated in a vacuum. The residue was treated with 250 ml of ether. The ethereal solution was washed with water and then with a solution of K_2CO_3 to a pH of the aqueous layer equal to 8-9 and dried with $MgSO_4$, the ether was evaporated, and the residue was chromatographed on 80 g of SiO_2 (180-210 mesh). Gradient elution by a hexane–ether mixture with ether contents from 5 to 50 vol. % yielded 6.8 g of V in the form of a light yellow oil, R_f 0.66 (1:1 ether–hexane). IR spectrum (ν, cm^{-1}): 530, 610, 720, 960, 1030, 1075, 1110, 1180, 1280, 1380, 1460, 1725, 3000 (film). PMR spectrum (δ, ppm): 1.99 d (J = 1.5 Hz, 3 H, CH_3), 4.60 s (2 H, CH_2S), 4.84 d. d (J = 1.5 and 7 Hz, 2 H, CH_2O), 5.87 br. t (J = 7 Hz, 1 H, C=CH), 7.5-8.0 m (5 H, C_6H_5).

N-[(Z)-4-Benzoyloxy-2-methylbut-2-ene-1-sulfonyl]pyrrolidine (VII). A 1.5-g portion (21 mmole) of pyrrolidine was added over the course of 5 min to a stirred solution of 2.9 g (10 mmole) of V in 60 ml of ether at 25°C. The precipitate formed was filtered and washed with CH_2Cl_2, the filtrate was evaporated, and the residue was crystallized from an ether–hexane mixture. This yielded 2.95 g (~ 95%) of VII in the form of colorless needles with mp 64-64.5°C. IR spectrum (ν, cm^{-1}): 710, 775, 805, 950, 1020, 1080, 1115, 1145, 1270, 1320, 1455, 1725 (KBr). PMR spectrum (δ, ppm): 2.0 m (7 H, CH_2CH_2 and CH_3), 3.39 m (4 H, CH_2N), 3.89 s (2 H, CH_2S), 4.9 d (J = 7 Hz, 2 H, CH_2O), 5.82 br. t (J = 7 Hz, 1 H, C=CH), 7.4-8.0 m (5 H, C_6H_5). Found: C 59.29; H 6.51; N 4.26; S 9.90%; M^+ 323. Calculated for $C_{16}H_{21}NO_4S$: C 59.43; H 6.55; N 4.33; S 9.92%; mol. wt. 323.4.

N-[(Z)-4-Benzoyloxy-2-methylbut-2-ene-1-sulfonyl]morpholine (VIII). In a similar manner 3.05 g (~90%) of VIII was obtained in the form of colorless needles with mp 113-114°C from 2.9 g (10 mmole) of V and 1.6 g (21 mmole) of morpholine. IR spectrum (ν, cm^{-1}): 730, 760, 855, 950, 1080, 1115, 1160, 1260, 1270, 1330, 1345, 1455, 1720 (KBr). PMR spectrum (δ, ppm): 2.01 d (J = 1.5 Hz, 3 H, CH_3), 3.34 m (4 H, CH_2N), 3.88 m (4 H, CH_2OCH_2), 4.0 s (2 H, CH_2S), 4.89 d (J = 7 Hz, 2 H, CH_2O), 5.84 br. t (J = 7 Hz, 1 H, C=CH), 7.5-8.0 m (5 H, C_6H_5). Found: C 56.12; H 6.44; N 4.47; S 9.48%; M^+ 339. Calculated for $C_{16}H_{21}NO_5S$: C 56.62; H 6.24; N 4.13; S 9.45%; mol. wt. 339.4.

N-[(E)-2-Methylbuta-1,3-diene-1-sulfonyl]pyrrolidine (VI). A solution of 3.2 g of VII and 0.56 g of KOH in 50 ml of 50% ethanol was boiled for 20 h, neutralized with HCl, concentrated in a vacuum, and extracted with ether. The extract was dried with $MgSO_4$ and evaporated, and the residue (3 g) was chromatographed on 150 g of SiO_2 (200 mesh). This yielded 0.65 g of VI in the form of colorless needles with mp 48-50°C (ether–hexane). IR spectrum (ν, cm^{-1}): 930, 1015, 1080, 1160, 1200, 1335, 1590, 2980 (CCl_4). UV spectrum (λ_{max}, nm): 243 (ε = 16,200) (EtOH). PMR spectrum (CCl_4, δ, ppm): 1.85 m (4 H, CH_2CH_2), 2.18 d (J = 1.3 Hz, 3 H, CH_3), 3.22 m (4 H, CH_2N), 5.33 br. d. d (J = 1.5 and 10.5 Hz, 1 H, HC^4), 5.58 br. d. d (J = 1.5 and 17 Hz, 1 H, HC^4), 6.07 br. q (J = 1.3 Hz, 1 H, HC^1), 6.38 br. d. d. d (J = 0.5, 10.5, and 17 Hz, 1 H, HC^3). Found: C 53.90; H 7.27; N 6.89; S 15.61%; M^+ 201. Calculated for $C_9H_{15}NO_2S$: C 53.76; H 7.41; N 6.96; S 15.94%; mol. wt. 201.1.

N-[(Z)-4-Hydroxy-2-methylbut-2-ene-1-sulfonyl]pyrrolidine (IX). A stirred solution of 3.2 g (10 mmole) of VII in 50 ml of THF at −25°C was given an addition of 12 ml of a 0.5 M solution of $LiAlH_4$ in THF (6 mmole) over the course of 2 min, stirred for 40 min at −20°C, and decomposed by H_2O in the presence of ether. The aqueous layer was neutralized and extracted with ether, the organic layer was dried with $MgSO_4$ and evaporated, and the residue (3.05 g) was chromatographed on 80 g of SiO_2 (200 mesh). Elution with ether yielded 1 g of $PhCH_2OH$, and elution with a 3:1 ether–acetone mixture yielded 2.0 g (~85%) of IX in the form of a colorless oil, R_f 0.25 (4:1 ether–acetone). IR spectrum (ν, cm^{-1}): 630, 920, 980, 1145, 1200, 1240, 1330, 3500 ($CHCl_3$). PMR spectrum (δ, ppm): 1.94 m (7 H, CH_2CH_2 and CH_3), 3.34 m (4 H, CH_2N), 3.84 s (2 H, CH_2S), 4.14 d. d (J = 1.5 and 7 Hz, 2 H, CH_2O), 5.72 br. t (J = 7 Hz, 1 H, C=CH).

N-[(Z)-4-Hydroxy-2-methylbut-2-ene-1-sulfonyl]morpholine (X). In a similar manner 2.1 g (~90%) of X in the form of colorless needles with mp 111-112°C (THF–ether–hexane) was obtained from 3.4 g (10 mmole) of VIII. IR spectrum (ν, cm^{-1}): 715, 760, 850, 945, 1020, 1035, 1075, 1110, 1160, 1275, 1330, 1345, 1450, 3400 (KBr). PMR spectrum (δ, ppm): 1.99 d (J = 1.5 Hz, 3 H, CH_3), 3.34 m (4 H, CH_2N), 3.74 m (6 H, CH_2S, CH_2OCH_2), 4.14 d (J = 7 Hz, 2 H, CH_2O), 5.88 br. t (J = 7 Hz, 1 H, C=CH). ^{13}C NMR spectrum (δ, ppm): 24.6 (CH_3), 45.9 (CH_2N), 50.9 (C^1), 58.9 (C^4), 66.5 (CH_2OCH_2), 126.2 (C^3), 132.9 (C^2). Found: C 45.97; H 7.25;

N 5.98; S 13.65%; M^+ 235. Calculated for $C_9H_{17}NO_4S$: C 45.94; H 7.28; N 5.95; S 13.63%; mol.wt. 235.3.

N-[(Z)-2-Methylbut-2-ene-1-sulfonyl]morpholine (XI). A stirred solution of 1.7 g (5 mmole) of VIII in 30 ml of THF at 0°C was given an addition of 6 ml of a 0.5 M solution of $LiAlH_4$ in THF (3 mmole) over the course of 2 min, stirred for 1 h at 0°C, and decomposed by H_2O in the presence of ether. The aqueous layer was neutralized and extracted with ether, the organic layer was dried with $MgSO_4$ and evaporated, and the residue (1.5 g) was chromatographed on 30 g of SiO_2 (200 mesh). Elution with a 1:1 ether–hexane mixture yielded 0.45 g of $PhCH_2OH$, and elution with ether yielded 0.95 g (~ 90%) of XI in the form of colorless prisms with mp 70-71°C (ether–hexane), which is identical to the specimen of XI described in [5].

(Z)-1-Methylsulfonyl-4-benzoyloxy-2-methylbut-2-ene (XIII). A stirred solution of 2.9 g (10 mmole) of V in 60 ml of ether at −50°C was given an addition of 22 ml (22 mmole) of a 1 M solution of PhMgBr in ether over the course of 10 min. The precipitate was filtered, washed with ether, and dried in a vacuum to constant weight. This yielded ~ 5 g of sulfinate XII in a mixture with Mg salts. PMR spectrum (CD_3CN, δ, ppm): 1.97 br. s (3 H, CH_3), 3.42 s (2 H, CH_2S), 5.06 d (J = 7 Hz, 2 H, CH_2O), 5.75 br. t (J = 7 Hz, 1 H, C=CH), 7.5-8.0 m (5 H, C_6H_5).

A solution of XII and 3 ml of MeI in 15 ml of DMF was stirred for 4 h at 50°C, diluted with H_2O, and extracted with ether. The usual treatment of the extract yielded ~ 2.6 g of a substance, which was chromatographed on 80 g of Al_2O_3 (activity level I-II). Elution with ether yielded 2.02 g (~ 75%) of XIII, which, when crystallized from a CH_2Cl_2–hexane mixture, yielded an analytical sample in the form of needles with mp 71.5-72°C. IR spectrum (ν, cm^{-1}): 715, 760, 810, 975, 1120, 1260, 1270, 1290, 1450, 1720 (KBr). PMR spectrum (δ, ppm): 1.98 br. s (3 H, CH_3), 2.92 s (3 H, SO_2CH_3), 3.96 s (2 H, CH_2S), 4.84 d (J = 7 Hz, 2 H, CH_2O), 5.84 br. t (J = 7 Hz, 1 H, C=CH), 7.5-8.0 m (5 H, C_6H_5). Found: C 58.30; H 6.09; S 11.82%; M^+ 268. Calculated for $C_{13}H_{16}O_4S$: C 58.19; H 6.01; S 11.95%; mol.wt. 268.3.

(Z)-1-(3'-Methylbut-2'-en-1'-yl)sulfonyl-4-benzoyloxy-2-methylbut-2-ene (XIV). In a similar manner 2.2 g (~80%) of XIV in the form of needles with mp 59-60°C (ether–hexane) were obtained from 2.9 g of V and 5.5 g of prenyl chloride. IR spectrum (ν, cm^{-1}): 960, 990, 1030, 1070, 1115, 1280, 1295, 1450, 1715 (KBr). PMR spectrum (δ, ppm): 1.74, 1.82, and 2.0 br. s (9 H, CH_3), 3.75 d (J = 7 Hz, 2 H, CH_2S), 3.9 s (2 H, CH_2S), 4.38 d (J = 7 Hz, 2 H, CH_2O), 5.32 br. t (J = 7 Hz, 1 H, C=CH), 5.86 br. t (J = 7 Hz, 1 H, C=CH), 7.4-8.0 m (5 H, C_6H_5). Found: C 63.25; H 6.82; S 9.59%. Calculated for $C_{17}H_{22}O_4S$: C 63.33; H 6.88; S 9.94%.

(Z)-1-Benzylsulfonyl-4-benzoyloxy-2-methylbut-2-ene (XV). In a similar manner 2.7 g (~ 80%) of XV in the form of needles with mp 104-105°C (CH_2Cl_2–hexane) was obtained from 2.9 g of V and 8.5 g of $PhCH_2Br$. IR spectrum (ν, cm^{-1}): 710, 785, 950, 1110, 1120, 1270, 1315, 1720 (KBr). PMR spectrum (δ, ppm): 1.92 br. s (3 H, CH_3), 3.82 s (2 H, CH_2S), 4.25 s (2 H, CH_2Ph), 4.72 d (J = 7 Hz, 2 H, CH_2O), 5.84 br. t (J = 7 Hz, 1 H, C=CH), 7.3-8.0 m (10 H, C_6H_5). Found: C 65.79; H 5.73; S 9.47%. Calculated for $C_{19}H_{20}O_4S$: C 66.25; H 5.85; S 9.31%.

(Z)-4-Methylsulfonyl-3-methylbut-2-en-1-ol (XVI). A solution of 2.7 g (10 mmole) of XIII in 50 ml of THF stirred at −25°C was given an addition of 12 ml of a 0.5 M solution of $LiAlH_4$ in THF (6 mmole), stirred for 40 min at −20°C, and treated as described above. The ethereal solution was dried by $MgSO_4$ and evaporated, and the residue (2.55 g) was chromatographed on 80 g of SiO_2 (200 mesh). Elution by ether yielded 1.05 g of $PhCH_2OH$, and elution with a 4:1 ether–acetone mixture yielded 1.57 g (~ 90%) of XVI in the form of a colorless oil, R_f 0.21 (4:1 ether–acetone). IR spectrum (ν, cm^{-1}): 970, 1010, 1130, 1140, 1245, 1310, 1415, 3030, 3500 ($CHCl_3$). PMR spectrum (δ, ppm): 1.92 d (J = 1.5 Hz, 3 H, CH_3), 2.94 s (3 H, CH_3S), 3.87 s (2 H, CH_2S), 4.12 d. d (J = 1.5 and 7 Hz, 2 H, CH_2O), 5.9 br. t (J = 7 Hz, 1 H, C=CH). ^{13}C NMR spectrum (δ, ppm): 24.1 (CH_3), 40.2 (CH_3S), 56.7 (C^4), 58.1 (C^1), 125.2 (C^3), 133.1 (C^2). M^+ 164. Calculated for $C_{16}H_{12}O_3S$: mol. wt. 164.2.

(Z)-4-(3'-Methylbut-2'-en-1'-yl)sulfonyl-3-methylbut-2-en-1-ol (XVII). In a similar manner 1.98 g (~ 90%) of XVII in the form of needles with mp 41-41.5°C (ether–hexane) was obtained from 3.2 g of XIV. IR spectrum (ν, cm^{-1}): 970, 1020, 1080, 1130, 1245, 1420, 3450 (KBr). PMR spectrum (δ, ppm): 1.76, 1.85, and 1.98 br. s (9 H, CH_3), 3.73 d (J = 7 Hz, 2 H, CH_2S), 3.80 s (2 H, CH_2S), 4.08 d (J = 7 Hz, 2 H, CH_2O), 5.32 br. t (J = 7 Hz, 1 H, C=CH), 5.95 br. t (J = 7 Hz, 1 H, C=CH). Found: C 55.03; H 8.03; S 14.76%. Calculated for $C_{10}H_{18}O_3S$: C 55.02; H 8.31; S 14.69%.

(Z)-4-Benzoyloxy-2-methylbut-2-ene-1-sulfonyl Azide (XVIII). A mixture of 2.9 g (10 mmole) of V and 1.3 g (20 mmole) of NaN_3 in 40 ml of MeCN was stirred for 20 h at 25°C, the filtrate was evaporated, and the residue was chromatographed on 100 g of SiO_2 (200 mesh). Elution with a 1:1 ether–hexane mixture yielded 1.98 g (70%) of XVIII in the form of a colorless oil, R_f 0.52 (1:1 ether–hexane). IR spectrum (ν, cm^{-1}): 900,

950, 1035, 1080, 1115, 1170, 1280, 1370, 1455, 1715, 3050 ($CHCl_3$). PMR spectrum (δ, ppm): 2.04 br. s (3 H, CH_3), 4.26 s (2 H, CH_2S), 4.86 d (J = 7 Hz, 2 H, CH_2O), 5.92 br. t (J = 7 Hz, 1 H, C=CH), 7.5-8.0 (5 H, C_6H_5). M^+ 295. Calculated for $C_{12}H_{13}N_3O_4S$: mol. wt. 295.3.

(Z)-Triphenylphosphazosulfonyl-4-benzoyloxy-2-methylbut-2-ene (XIX). A solution of 1.32 g (5 mmole) of PPh_3 in 15 ml of THF was added over the course of 3 min to a solution of 1.48 g (5 mmole) of XVIII in 30 ml of THF stirred at 25°C. After cessation of the evolution of N_2 (~ 15 min), the solution was evaporated, and the residue was chromatographed on 50 g of SiO_2 (150 mesh). Elution with ether yielded 2.52 g (95%) of XIX in the form of a viscous colorless mass, R_f 0.65 (ether). IR spectrum (ν, cm^{-1}): 500, 530, 610, 715, 725, 1030, 1115, 1180, 1280, 1715 ($CHCl_3$). PMR spectrum (δ, ppm): 1.74 s (3 H, CH_3), 3.66 s (2 H, CH_2S), 4.63 d (J = 7 Hz, 2 H, CH_2O), 5.48 br. t (J = 7 Hz, 1 H, C = CH), 7.50 m (20 H, C_6H_5). M^+ 529. Calculated for $C_{30}H_{28}NO_4PS$: mol. wt. 529.6.

(Z)-Triphenylphosphazosulfonyl-4-hydroxy-2-methylbut-2-ene (XX). A solution of 1.05 g (2 mmole) of XIX in 25 ml of THF stirred at −25°C was given an addition of 2 ml of a 0.6 M solution of $LiAlH_4$ in THF (1.2 mmole) over the course of 2 min, stirred for 40 min at −20°C, and treated as described above. The ethereal solution was dried with $MgSO_4$ and evaporated, and the residue (0.87 g) was chromatographed on 50 g of SiO_2 (200 mesh). Elution with a 3:1 ether–acetone mixture yielded 410 mg (48%) of XX in the form of colorless needles with mp 134-135°C (THF–ether–hexane). IR spectrum (ν, cm^{-1}): 530, 560, 610, 730, 1000, 1030, 1120, 1150, 1270, 1340, 3070, 3430 (KBr). PMR spectrum (δ, ppm): 1.72 s (3 H, CH_3), 3.54 s (2 H, CH_2S), 3.73 d (J = 7 Hz, 2 H, CH_2O), 5.56 br. t (J = 7 Hz, 1 H, C = CH), 7.5 m (15 H, C_6H_5). Found: C 65.08; H 5.72; N 3.39; S 7.48%; M^+ 425. Calculated for $C_{23}H_{24}NO_3PS$: C 64.94; H 5.68; N 3.29; S 7.53%; mol. wt. 425.7.

CONCLUSIONS

The stereospecific transformation of a β,γ-unsaturated δ-sultone into derivatives of (Z)-4-hydroxy-2-methylbut-2-ene-1-sulfonic acid has been carried out.

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