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2,5-Dichloro-4,4-ethylenedioxy-3-phenylsulfonyl-2-cyclopentenone in Nucleophilic Substitution and Addition Reactions

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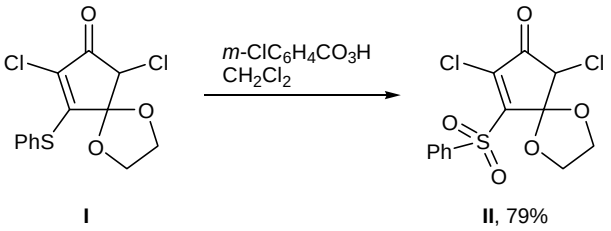
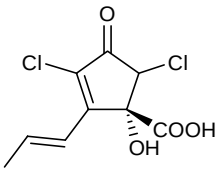
Abstract—2,5-Dichloro-4,4-ethylenedioxy-3-phenylsulfonyl-2-cyclopentenone reacts with diethyl malonate potassium salt according to the Ad_NE pattern with replacement of chlorine atoms at the double C=C bond, while the reaction of the same substrate with allylcuprate is not selective, and it follows several pathways.

Oxidation of previously described 2,5-dichloro-4,4-ethylenedioxy-3-phenylsulfanyl-2-cyclopentenone (**I**) [1] with *m*-chloroperoxybenzoic acid gave sulfone **II** (Scheme 1) which is an intriguing example of polyfunctional cyclopentenone electrophiles. The behavior of sulfone **II** in reactions with nucleophiles is difficult to predict. With a view to subsequently use sulfone **II** in purposeful syntheses, specifically in the development of synthetic approaches to the natural antibiotic cryptosporiopsin (**III**) [2, 3], it was necessary to elucidate chemo-, regio-, and stereoselectivity aspects in nucleophilic substitution and 1,2-addition involving the C^1, C^2, and C^3 sp^2-hybridized centers, respectively.

Scheme 1.



I **II**, 79%

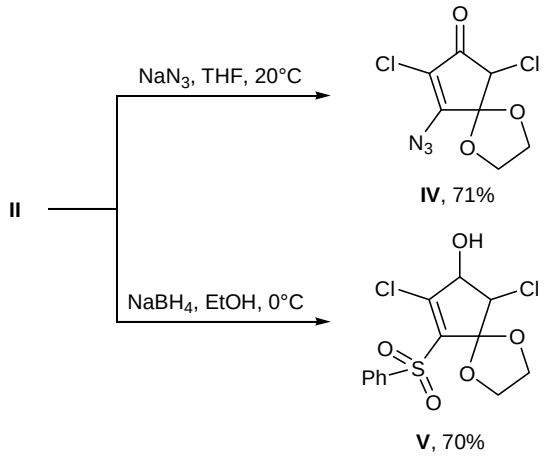


III

In order to estimate the reactivity of the enone fragment we examined first reactions of sulfone **II** with NaN_3 and $NaBH_4$. In the reaction with NaN_3, azide **IV** was formed exclusively as a result of replacement of the phenylsulfonyl group on C^3 (Scheme 2). The activated C^2=C^3 double bond remained intact in the reduction of **II** with $NaBH_4$, and the product was alcohol **V** which was formed with high stereoselectivity. The *cis* arrangement of the OH and Cl substituents in molecule **V** follows from the ^{1}H NMR spectrum where the 1-H and 5-H signals appeared as doublets with a coupling constant ^3J of 6.6 Hz [4]. Our results indicate an appreciable polarization of the double C=C bond (addition of azide ion at C^3) and electrophilicity of the carbonyl group (no enolization was observed during the reduction with sodium tetrahydridoborate).

While developing synthetic approaches to precursors of **III**, we studied reactions of sulfone **II** with diethyl malonate potassium salt and allylcuprate reagent [5]. The reaction of **II** with diethyl malonate

Scheme 2.



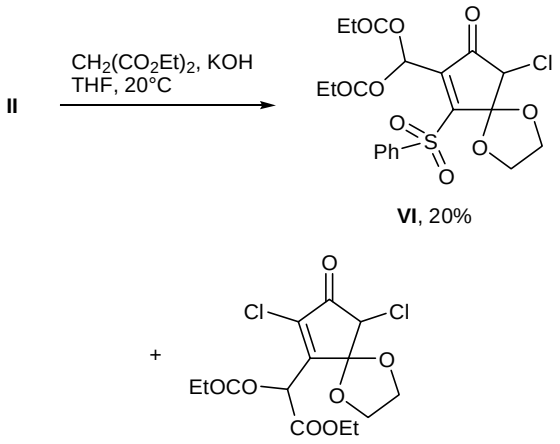
IV, 71%

V, 70%

1070-4280/05/4104-0551

potassium salt as one of the most practical C-nucleophiles gave a mixture of two Ad_NE-substitution products at the sp^2-hybridized carbon atoms (replacement of the $PhSO_2$ group and Cl atom), compounds **VI** and **VII** at a ratio of 2:5 (Scheme 3). This ratio indicates more ready replacement of the phenylsulfonyl group as compared to Cl. The formation of compound **VI** is an unusual example of substitution at C^2 in such systems [6].

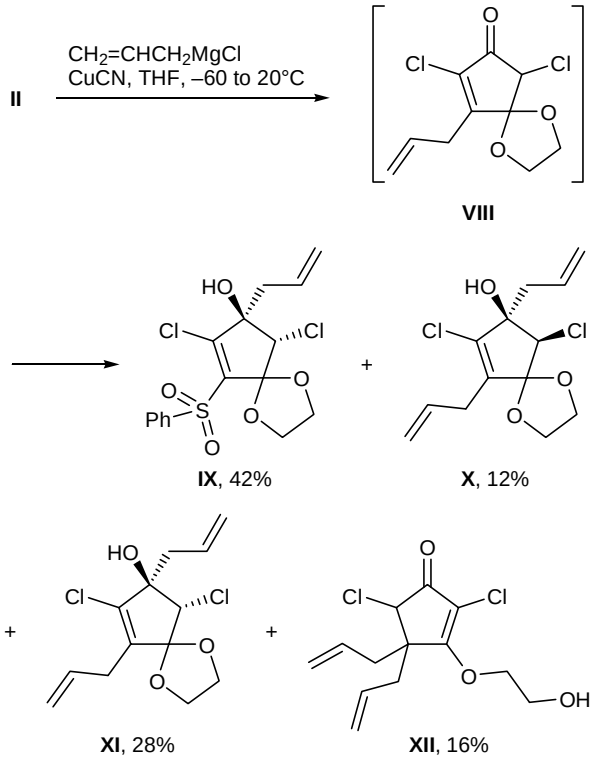
Scheme 3.



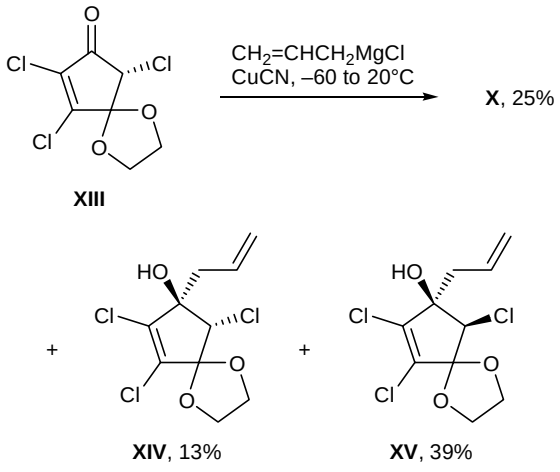
An unusual pattern was also observed in the reaction of phenyl sulfone **II** with allylcuprate reagent CH_2=$CHCH_2MgCl$/CuCN, which led to formation of a mixture of compounds **IX**–**XII** in high yield (Scheme 4). Here, the substitution at C^3 was accompanied by 1,2-addition at the carbonyl group of **II** (compound **IX**), and the anticipated primary 1,4-addition product **VIII** reacted further to give a mixture of compounds **X**–**XII**. It should be noted that the observed pattern is not typical of cuprate reactions with enones [7], although Vostrikov *et al*. [8] previously reported on an anomalous reaction of 2,3,5-trichloro-4,4-ethylenedioxy-2-cyclopentenone (**XIII**) with lithium dimethylcuprate, which afforded (*Z*)-2,4,5-trichloro-3,3-ethylenedioxy-4-pentenoic and (*Z*)-2,5-dichloro-3,3-ethylenedioxy-4-pentenoic acids as the major products.

We performed the reaction of trichloro-substituted enone **XIII** with allylcuprate reagent under the same conditions as in the reaction with sulfone **II** with a view to compare their reactivities. In this case, the main reaction pathway (2:1) was 1,2-addition of the allyl nucleophile at the carbonyl group of cyclopentenone **XIII** to give a mixture of stereoisomeric adducts **XIV** and **XV** (Scheme 5). Analogous pattern was observed previously for reactions of enone **XIII** and structurally related cyclopentenones with lithium, magnesium, and zinc reagents which are more active than cuprates [7–9].

Scheme 4.



Scheme 5.



Stereoisomeric chlorocyclopentenols **X**/**XI** and **XIV**/**XV** and enone **VIII** characteristically showed in the ^{13}C NMR spectra signals from the C^5 atom and methylene carbon atom of the neighboring allyl group. Due to steric contraction effect, these signals in the spectra of *trans* isomers **XI** and **XIV** appear in

a stronger field relative to the corresponding signals of *cis* isomers **X** and **XV**. In addition, an appreciable difference in the chemical shifts of diastereotopic methylene protons in the allyl group was observed in the ^{1}H NMR spectra of *trans* isomers **XI** and **XIV**.

EXPERIMENTAL

The IR spectra were recorded on UR-20 and Specord M-80 instruments from samples prepared as thin films or dispersed in mineral oil. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-300 spectrometer at 300.13 and 75.47 MHz, respectvely, using $CDCl_3$ as solvent and reference (δ 7.27 ppm, δ_C 77.00 ppm). The mass spectra (electron impact, 20 or 70 eV) were recorded on an MKh-1306 mass spectrometer (ion source temperature 75–100°C). The progress of reactions and the purity of products were monitored by TLC on Silufol plates using petroleum ether–ethyl acetate as eluent; spots were detected by treatment with an alkaline solution of $KMnO_4$ [10].

2,5-Dichloro-4,4-ethylenedioxy-3-phenylsulfonyl-2-cyclopentenone (II). A solution of 1.50 g (4.73 mmol) of sulfide **I** in 15 ml of methylene chloride was added dropwise at 0°C to a suspension of 5.38 g (15.60 mmol) of 50% *m*-chloroperoxybenzoic acid in 20 ml of methylene chloride. The mixture was stirred for 1.5 h and filtered, and the filtrate was diluted with 30 ml of methylene chloride and washed with water. The aqueous phase was extracted with 30 ml of methylene chloride, and the extract was combined with the organic phase, washed with a solution of $NaHCO_3$ until neutral washings, dried over $MgSO_4$, and evaporated. The residue was recrystallized from ethyl acetate to obtain 1.30 g (79%) of sulfone **II** as a colorless crystalline substance, mp 122°C. IR spectrum, ν, cm^{-1}: 1765, 1600, 1340, 1160, 1040. ^{1}H NMR spectrum, δ, ppm: 4.43 m (4H, CH_2O), 4.48 m (2H, CH_2O), 4.58 s (1H, 5-H), 7.60 t (2H, *m*-H, *J* = 7.56 Hz), 7.72 t (1H, *p*-H, *J* = 7.56 Hz), 8.04 t (2H, *o*-H, *J* = 7.56 Hz). ^{13}C NMR spectrum, δ_C, ppm: 63.36 (C^5), 67.51 (CH_2O), 109.31 (C^4), 128.62 (C^o), 129.30 (C^p), 134.95 (C^i), 138.96 (C^m), 140.77 (C^2), 155.45 (C^3), 187.57 (C^1). Found, %: C 44.32; H 3.03; Cl 20.16; S 9.24. $C_{13}H_{10}Cl_2O_5S$. Calculated, %: C 44.72; H 2.89; Cl 20.31; S 9.18.

3-Azido-2,5-dichloro-4,4-ethylenedioxy-2-cyclopentenone (IV). Sodium azide, 0.08 g (1.15 mmol), was added at 20°C to a solution of 0.20 g (0.57 mmol) of sulfone **II** in 5 ml of THF. The mixture was stirred for 1.5 h, diluted with ethyl acetate, washed with water and a saturated solution of sodium chloride, dried over $MgSO_4$, and evaporated, and the residue was subjected to column chromatography on silica gel using petroleum ether–ethyl acetate (9:1) to isolate 0.10 g (71%) of compound **IV** as a colorless crystalline substance, mp 95–97°C. IR spectrum, ν, cm^{-1}: 1752, 1620. ^{1}H NMR spectrum, δ, ppm: 4.29 t (2H, CH_2O, *J* = 6.5 Hz), 4.39 t (2H, CH_2O, *J* = 6.5 Hz), 4.48 s (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 61.50 (C^5), 66.36 (CH_2O), 107.08 (C^4), 119.50 (C^2), 156.88 (C^3), 191.11 (C^1). Found, %: C 33.2; H 2.00; Cl 28.12; N 16.50. $C_7H_5Cl_2N_3O_3$. Calculated, %: C 33.63; H 2.02; Cl 28.36; N 16.81.

2,5-Dichloro-4,4-ethylenedioxy-3-phenylsulfonyl-2-cyclopentenol (V). Sodium tetrahydridoborate, 0.005 g (0.14 mmol), was added at 0°C to a solution of 0.10 g (0.28 mmol) of sulfone **II** in 4 ml of a 1:1 EtOH–THF mixture. The mixture was stirred for 1 h, 0.30 ml of 10% hydrochloric acid was added, and the mixture was evaporated. The residue was treated with 2 ml of water and extracted with chloroorm. The extract was washed with a 10% solution of $NaHCO_3$, dried over $MgSO_4$, and evaporated, and the residue was subjected to column chromatography on silica gel using petroleum ether–ethyl acetate (9:1) as eluent to isolate 0.07 g (70%) of alcohol **V** as a colorless crystalline substance, mp 119°C. IR spectrum, ν, cm^{-1}: 3410, 1605, 1345, 1020. ^{1}H NMR spectrum, δ, ppm: 4.16–4.26 m (4H, CH_2O, *J* = 6.36 Hz), 4.33 (1H, H), 4.48 br.s (1H, 4-H), 7.55 t (2H, *m*-H, *J* = 7.50 Hz), 7.66 t (1H, *p*-H, *J* = 7.50 Hz), 8.00 t (2H, *o*-H, *J* = 7.50 Hz). ^{13}C NMR spectrum, δ_C, ppm: 65.42 (C^5), 66.75 and 67.34 (CH_2O), 74.33 (C^1), 113.77 (C^4), 127.98 (C^p), 129.02 (C^o), 134.04 (C^m), 138.77 (C^i), 140.39 (C^3), 149.13 (C^2). Found, %: C 44.64; H 3.53; Cl 20.25; S 9.18. $C_{13}H_{12}Cl_2O_5S$. Calculated, %: C 44.46; H 3.44; Cl 20.19; S 9.13.

Reaction of sulfone II with diethyl malonate potassium salt. Potassium hydroxide, 0.27 g (4.73 mmol), and diethyl malonate, 0.65 ml (4.3 mmol), were added at room temperature to a solution of 0.30 g (0.86 mmol) of sulfone **II** in 8 ml of THF. The mixture was stirred for 20 min, 25 ml of ethyl acetate and 5 ml of 10% hydrochloric acid were added, the organic phase was separated, and the aqueous phase was extracted with ethyl acetate (3× 25 ml). The extracts were combined with the organic phase, washed with 10% hydrochloric acid (until neutral washings, pH 7) and a saturated solution of sodium chloride, dried over $MgSO_4$, and evaporated. The residue was subjected to column chromatography

on silica gel using petroleum ether–ethyl acetate (9:1) as eluent to isolate 0.08 g (20%) of compound **VI** and 0.16 g (51%) of **VII**.

Diethyl 2-(4-chloro-3,3-ethylenedioxy-2-phenylsulfonyl-5-oxo-1-cyclopentenyl)propanedioate (VI). Yellow oily substance, R_f 0.16 (petroleum ether–ethyl acetate, 8:2, 4 runs). IR spectrum, ν, cm^{-1}: 1045, 1165, 1340, 1590, 1728, 1752. ^1H NMR spectrum, δ, ppm: 1.21 t (3H, CH_3, J = 6.98 Hz), 2.75 s (2H, CH_2), 4.13 q (2H, CH_2O, J = 6.9 Hz), 4.15 q (2H, CH_2O, J = 7.2 Hz), 3.99 m [4H, $(CH_2O)_2$, J = 8.03 Hz], 4.24 m [4H, $(CH_2O)_2$, J = 8.03 Hz], 5.38 s (1H, CH), 7.56 d.d (2H, *m*-H, J = 7.84, 7.38 Hz), 7.67 d.d (2H, *o*-H, J = 7.40, 7.23 Hz), 7.97 d (1H, *p*-H, J = 7.86 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.91 (CH_3), 48.39 (C^4), 62.40 (**C**H_2CH_3), 66.44 (CH_2O), 111.24 (C^3), 128.05 (C^o), 129.27 (C^p), 134.43 (C^m), 140.51 (C^i), 145.42 (C^1), 158.91 (C^2), 164.99 (COO), 198.01 (C^5). Found, %: C 50.62; H 4.30; Cl 7.70; S 6.43. $C_{20}H_{21}ClO_9S$. Calculated, %: C 50.80; H 4.48; Cl 7.50; S 6.78.

Diethyl 2-(2,4-dichloro-5,5-ethylenedioxy-3-oxo-1-cyclopentenyl)propanedioate (VII). Yellow crystalline substance, mp 85–88°C, R_f 0.25 (petroleum ether–ethyl acetate, 8:2, 4 runs). IR spectrum, ν, cm^{-1}: 1045, 1165, 1320, 1470, 1730, 1752, 2936. ^1H NMR spectrum, δ, ppm: 1.21–1.26 m (6H, $2CH_3$), 4.08–4.25 m (8H, CH_2O, C**H**$_2CH_3$), 4.43 s (1H, 4-H), 4.47 s (1H, $CHCO_2$). ^{13}C NMR spectrum, δ_C, ppm: 14.05 (CH_3), 49.51 (**C**HCO_2), 61.41 (C^4), 62.47 (CH_3**C**H_2O), 66.75 (CH_2O), 108.51 (C^5), 136.91 (C^2), 153.49 (C^1), 164.36 (COO), 188.75 (C^3). Found, %: C 46.10; H 4.25; Cl 19.50. $C_{14}H_{16}Cl_2O_7$. Calculated, %: C 45.80; H 4.39; Cl 19.31.

Reaction of sulfone II with allylmagnesium chloride. Copper(I) cyanide, 0.01 g (0.95 mmol), was added under argon to 7 ml of a 0.6 M solution of allylmagnesium chloride (4.30 mmol) in THF, and the mixture was stirred for 20 min. The mixture was then cooled to –60°C, and a solution of 0.30 g (0.95 mmol) of sulfone **II** in 10 ml of THF was slowly added in a dropwise manner. The mixture was stirred or 1 h at 0°C (until complete conversion of sulfone **II**), treated with 5 ml of a saturated solution of ammonium chloride, and extracted with ethyl acetate. The combined extracts were washed with a saturated solution of sodium chloride, dried over $MgSO_4$, and evaporated, and the residue was subjected to column chromatography on silica gel using petroleum ether–ethyl acetate (95:5) as eluent to isolate 0.14 g (42%) of compound **IX**, 0.03 g (12%) of **X**, 0.07 g (28%) of **XI**, and 0.04 g (16%) of **XII**.

(1*S*,5*S*)-1-Allyl-2,5-dichloro-4,4-ethylenedioxy-3-phenylsulfonyl-2-cyclopentenol (IX). Yellow oily substance, R_f 0.49 (petroleum ether–ethyl acetate, 1:1). IR spectrum, ν, cm^{-1}: 1040, 1220, 1340, 1590, 1610, 3020, 3080, 3460. ^1H NMR spectrum, δ, ppm: 2.44–2.46 m (2H, 1'-H), 4.21 s (1H, OH), 4.27 t (1H, 6-H), 4.15–4.54 m (4H, CH_2O), 4.24 s (1H, 5-H), 5.11–5.21 m (2H, 3'-H), 5.46 m (1H, 2'-H), 7.56 t (2H, *m*-H, J = 7.3 Hz), 7.67 t (1H, *p*-H, J = 7.1 Hz), 7.99 t (2H, *o*-H, J = 7.9 Hz). ^{13}C NMR spectrum, δ, ppm: 38.61 ($C^{1'}$), 66.24 (C^5), 67.29 (CH_2O), 79.54 (C^1), 113.13 (C^4), 121.37 ($C^{3'}$), 127.55 (C^o), 128.73 (C^p), 130.12 (C^m), 133.87 ($C^{2'}$), 139.05 (C^3), 140.04 (C^i), 151.39 (C^2). Found, %: C 49.23; H 4.05; Cl 18.08; S 8.11. $C_{16}H_{16}Cl_2O_5S$. Calculated, %: C 49.12; H 4.12; Cl 18.12; S 8.20.

(1*R*,5*S*)-1,3-Diallyl-2,5-dichloro-4,4-ethylenedioxy-2-cyclopentenol (X). Yellow oily substance, R_f 0.35 (petroleum ether–ethyl acetate, 9:1, 2 runs). IR spectrum, ν, cm^{-1}: 748, 784, 1204, 1636, 3448. ^1H NMR spectrum, δ, ppm: 2.56–2.69 m (2H, 1'-H), 2.58 br.s (1H, OH), 2.92–2.94 m (2H, 1''-H), 3.98–4.09 m (4H, CH_2O), 4.19–4.24 (2H, 3''-H), 4.36 s (1H, 5-H), 5.03–5.06 m (2H, 3'-H), 5.19 m (1H, 2''-H), 5.75 m (1H, 2'-H). ^{13}C NMR spectrum, δ_C, ppm: 38.85 (C^{12}), 66.58 (C^6), 67.56 (CH_2O), 79.82 (C^7), 113.44 (C^2), 121.64 (C^{14}), 134.20 (C^{13}), 151.39 (C^7). Found, %: C 53.32; H 5.68; Cl 24.18. $C_{13}H_{16}Cl_2O_3$. Calculated, %: C 53.62; H 5.54; Cl 24.35.

(1*S*,5*S*)-1,3-Diallyl-2,5-dichloro-4,4-ethylenedioxy-2-cyclopentenol (XI). Yellow oily substance, R_f 0.30 (petroleum ether–ethyl acetate, 9:1, 2 runs). IR spectrum, ν, cm^{-1}: 748, 784, 1204, 1636, 3448. ^1H NMR spectrum, δ, ppm: 2.43–2.62 m (2H, 1'-H), 2.48 br.s (1H, OH), 2.93–2.94 m (2H, 1''-H), 3.98–4.14 m (4H, CH_2O), 4.20–4.23 (2H, 3''-H), 4.29 s (1H, 5-H), 5.03–5.06 m (2H, 3'-H), 5.19 m (1H, 2''-H), 5.75 (1H, 2'-H). ^{13}C NMR spectrum, δ_C, ppm: 29.17 ($C^{1''}$), 38.96 ($C^{1'}$), 66.28 (C^6), 66.61 (CH_2O), 79.37 (C^7), 113.10 (C^5), 116.31 ($C^{3'}$), 120.48 ($C^{3'}$), 131.65 ($C^{2''}$), 133.09 ($C^{2'}$), 136.18 (C^9), 139.04 (C^8). Found, %: C 53.32; H 5.68; Cl 24.18. $C_{13}H_{16}Cl_2O_3$. Calculated, %: C 53.62; H 5.54; Cl 24.35.

4,4-Diallyl-2,5-dichloro-3-(2-hydroxyethoxy)-2-cyclopentenone (XII). Yellow oily substance, R_f 0.26 (petroleum ether–ethyl acetate, 1:1). IR spectrum, ν, cm^{-1}: 935, 1020, 1070, 1580, 1600, 1728, 3090, 3400. ^1H NMR spectrum, δ, ppm: 2.15–2.61 m (4H, 1'-H, 1''-H), 3.77 m (1H, OH), 3.95 t (2H, C**H**$_2$OH, J = 4.42 Hz), 4.47 s (1H, 5-H), 4.74–4.87 m (2H, CH_2O), 5.06–5.25 m (4H, 3'-H, 3''-H), 5.13 m (2H, 6-H), 5.03

and 5.06 (2H, 3'-H, J = 1.20, 2.83 Hz), 5.19 (1H, 2"-H), 5.75 (1H, 2'-H, 2"-H). ^{13}C NMR spectrum, δ_C, ppm: 39.27 ($C^{1'}$), 40.70 ($C^{1''}$), 66.33 (C^5), 61.19 (CH_2OH), 73.99 (CH_2O), 106.02 (C^2), 119.41 ($C^{3'}$), 120.97 ($C^{3''}$), 131.77 ($C^{2'}$), 132.51 ($C^{2''}$), 178.32 (C^3), 191.05 (C^1). Found, %: C 53.43; H 5.58; Cl 24.21. $C_{13}H_{16}Cl_2O_3$. Calculated, %: C 53.62; H 5.54; Cl 24.35.

Reaction of trichlorocyclopentenone XIII with allylmagnesium chloride. Copper(I) cyanide, 0.01 g (0.95 mmol), was added under argon to a 0.6 M solution of allylmagnesium chloride in THF, 7 ml (4.30 mmol), and the mixture was stirred for 20 min. The mixture was then cooled to –15°C, a solution of 0.30 g (1.23 mmol) of ketone **XIII** in 10 ml of THF was slowly added in a dropwise manner, and the mixture was stirred for 1 h at 0°C and for 12 h at room temperature, cooled to 0°C, treated with 5 ml of a saturated solution of ammonium chloride, and extracted with ethyl acetate. The combined extracts were washed with a saturated solution of sodium chloride, dried over $MgSO_4$, and evaporated, and the residue was subjected to column chromatography on silica gel using petroleum ether–ethyl acetate (99:1) as eluent to isolate 0.08 g (25%) of compound **X**, 0.05 g (13%) of **XIV**, and 0.15 g (39%) of **XV**.

(1*S*,5*S*)-1-Allyl-2,3,5-trichloro-4,4-ethylenedioxy-2-cyclopentenol (XIV). Colorless oily substance, R_f 0.27 (petroleum ether–ethyl acetate, 95:5, 2 runs). IR spectrum, ν, cm^{-1}: 800, 819, 928, 1258, 1636, 3430. ^{1}H NMR spectrum, δ, ppm: 2.45–2.62 m (2H, 1'-H), 2.70 s (1H, OH), 4.10–4.25 m (4H, CH_2O), 4.34 s (1H, 5-H), 5.19–5.23 (2H, 3'-H), 5.6 m (1H, 2'-H). ^{13}C NMR spectrum, δ_C, ppm: 39.26 ($C^{1'}$), 64.82 (C^5), 66.84 and 67.56 (CH_2O), 78.97 (C^1), 110.78 (C^4), 121.19 ($C^{3'}$), 130.99 ($C^{2'}$), 133.46 (C^3), 137.58 (C^2). Found, %: C 42.23; H 3.53; Cl 37.08. $C_{10}H_{11}Cl_3O_3$. Calculated, %: C 42.06; H 3.88; Cl 37.25.

(1*R*,5*S*)-1-Allyl-2,3,5-trichloro-4,4-ethylenedioxy-2-cyclopentenol (XV). Colorless oily substance, R_f 0.21 (petroleum ether–ethyl acetate, 95:5, 2 runs). IR spectrum, ν, cm^{-1}: 824, 930, 1255, 1630, 3430. ^{1}H NMR spectrum, δ, ppm: 2.57–2.68 (2H, 3'-H), 2.70 s (1H, OH), 4.10–4.25 m (4H, CH_2O), 4.42 s (1H, 5-H), 5.24–5.28 m (2H, 3'-H), 6.00 m (1H, 2'-H). ^{13}C NMR spectrum, δ_C, ppm: 41.55 ($C^{1'}$), 66.79 and 67.12 (CH_2O), 70.51 (C^5), 79.62 (C^1), 109.62 (C^4), 121.29 ($C^{3'}$), 130.85 ($C^{2'}$), 131.58 (C^3), 138.74 (C^2). Found, %: C 42.23; H 3.53; Cl 37.08. $C_{10}H_{11}Cl_3O_3$. Calculated, %: C 42.06; H 3.88; Cl 37.25.

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