Aspects of stereoselectivity in electrophilic addition reactions of iodine with 5-allenyl-2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-one and its derivatives

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The reactions of 5-allenyl-2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-one and related compounds with I_2 were studied. The stereochemistry of the resulting 1,2-adducts with I_2 at the terminal double bond of the allenic fragment depends in a complex way on the character of functionalization in the cyclopentene fragment of the starting molecule.

Key words: allenes, iodination, isomerism.

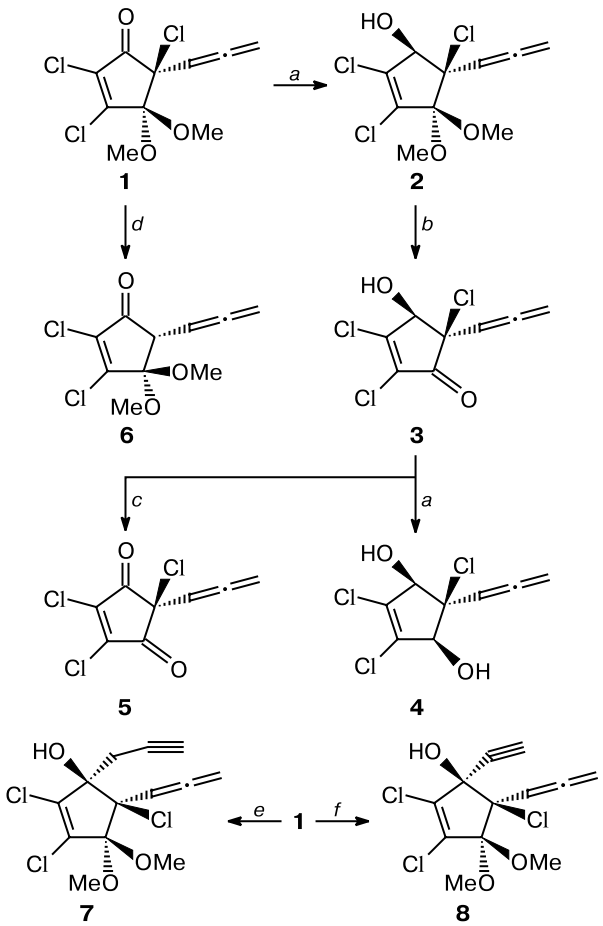
Reactions of functionalized allenes with I_2 are of interest from the viewpoint of studying the stereoselectivity of 1,2-addition of electrophiles.[1—3] However, these reactions have not been adequately investigated. In this connection, we examined electrophilic iodination of allenylcyclopentenone (**1**)[4] and its derivatives (**2—8**) presented in Scheme 1. Another purpose of the present study was to develop a route to the corresponding iodoallylcyclopentenones, which can be involved in subsequent intramolecular Barbier-type cyclizations.

The syntheses and stereochemistry of *cis*-chlorohydrins **2**[5] and **7**,[6] allene **6**,[7] and related compounds have been reported in our earlier studies.[8,9]*

As regards the stereochemistry of the reactions used for the synthesis of compound **2—8**, it should be noted that in these systems the Cl atom at C(5) exerts an efficient steric control over the direction of the attack of the hydride (or organometallic) reagent giving rise exclusively (>95%) to *cis*-chlorohydrins **5—9**. Hence, we believe that the stereochemistry of newly synthesized compounds **4** and **8** corresponds to that shown in Scheme 1.

When studying the reaction of allenylcyclopentenone **1** with I_2 in CH_2Cl_2, we found that it afforded thermodynamically less favorable *E*-diiodide (**9**) as the major product (**9** : **10** = 86 : 14) (Scheme 2). The fact that isomer **10** is energetically more favorable is evidenced by isomerization of individual compound **9** into **10**, which readily proceeded upon heating over a short period of time (storage of **9** at 50 °C for 30 min afforded a mixture of **9** and **10** in a ratio of 6 : 4). The use of other solvents (MeCN or MeOH) for iodination of **1** had no effect on the ratio and

Scheme 1



Reagents and conditions: *a*. $NaBH_4$, MeOH, 20 °C; *b*. H_3O^+; *c*. H_2CrO_4, $Me_2CO—H_2O$; *d*. $CrCl_2$, $Me_2CO—H_2O$; *e*. $HC{\equiv}CCH_2MgBr$, THF; *f*. $HC{\equiv}CMgBr$, THF.

* Hereinafter, the structural formulas of only one of enantiomers are given. In all experiments, racemic mixtures were used.

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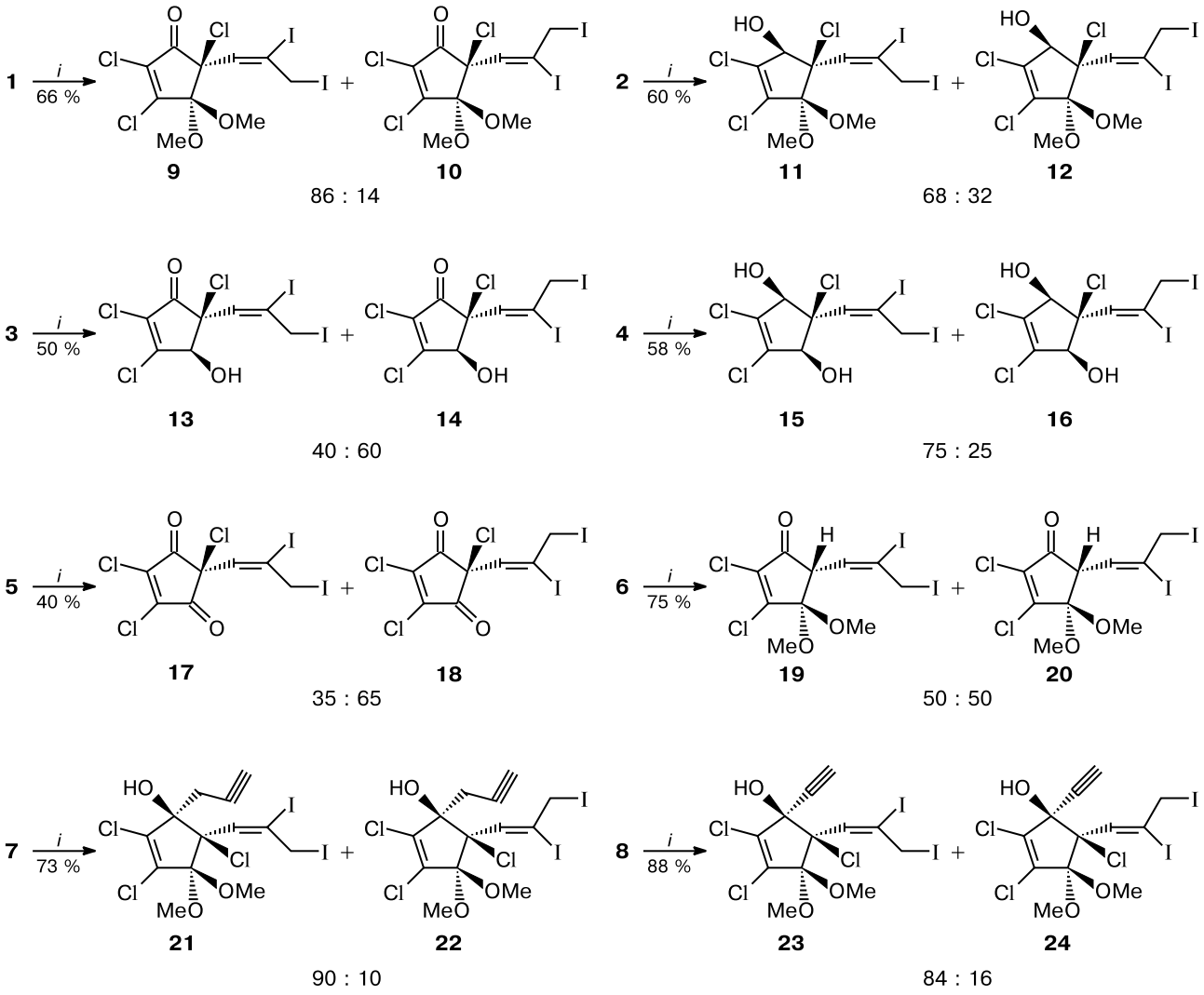
Scheme 2



i. 1.1 equiv., I_2, CH_2Cl_2, 20 °C.

total yield of isomers **9** and **10**. Therefore, we also carried out iodination of compounds **2—8** in CH_2Cl_2.

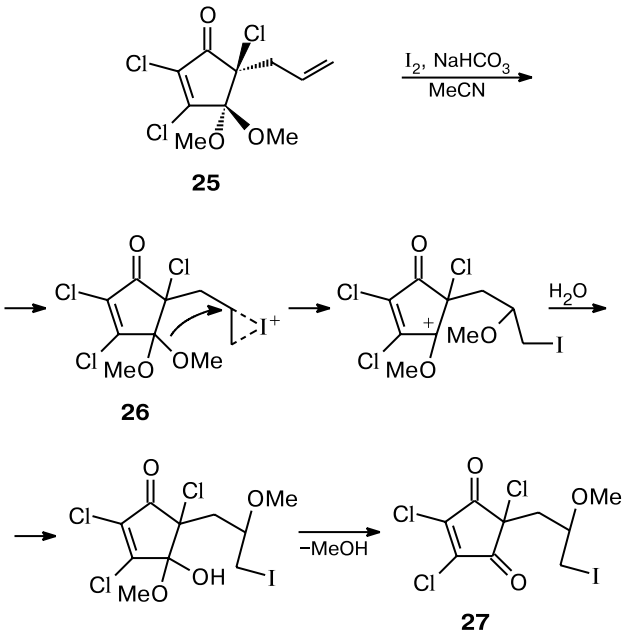
The stereoselectivity of the reaction of dimethoxyalcohol **2** with I_2 is somewhat worse (**11** : **12** = 68 : 32) although it is similar to that observed in the reaction of allene **1**. Iodination of diol **4** and *cis*-chlorohydrins **7** and **8** afforded the corresponding diiodides in ratios similar to those obtained in the reactions of **1** and **2**. By contrast, the ratio between the reaction products in the case of keto alcohol **3** and diketone **5** changed in favor of the corresponding *Z* isomers, whereas iodination of C(5)-dechlorinated allene **6** proceeded nonstereoselectively (*Z* : *E* = 1 : 1). It is interesting that the ratio between the isomers of iodides changed in the course of acid hydrolysis of a mixture of dimethoxyalcohols **11—12** (68 : 32) giving rise to a mixture of keto alcohols **13—14** in a ratio of 32 : 68.

The diiodides were isolated in the individual form by column chromatography on SiO_2 or recrystallization. The isomer ratios in the mixtures were determined from the integral intensities of singlets of the olefinic protons in the ^1H NMR spectra of the reaction mixtures before their purification by chromatography or recrystallization. In the ^1H NMR spectra, the signals of the vinylic protons of *E*-diiodides are generally observed at higher field[10] than the signals of the corresponding *Z* isomers although the chemical shifts of the vinylic protons depend substantially on the presence of other substituents at the double bond. In addition, we found that the chemical shifts of the diastereotopic protons of the CH_2I group in the *E* isomers

differ substantially from each other (by ~0.4 ppm), whereas this difference for *Z*-diiodides is generally less significant (<0.01 ppm). In the ^{13}C NMR spectra, the signals of the CH_2I groups are most informative for assigning isomeric diiodides to either the *Z* or *E* series; due to the ^{13}C-steric compression effect for *E* isomers, these signals are characterized by the largest upfield shifts.[11—13] Hence, we used this criterion in controversial cases for the assignment of isomers to either the *Z* or *E* series.

At first glance, the stereochemical result of the addition of I_2 to compound **1** and related allenes is difficult to explain. The conditions of all experiments were identical. The only difference is in the functionalization of the cyclopentene fragment of these molecules. In this connection, it should be noted that earlier we have found the anchimeric assistance of the MeO group to iodination of 5-allylcyclopentenone (**25**) in MeCN, which is accompanied by migration of one of the MeO groups to the side chain. Apparently, this is attributable to the fact that the MeO group is in proximity to positive iodonium cation **26** and, hence, can be coordinated by the latter followed by migration of the MeO group to the side chain giving rise to dione (**27**)[14] (Scheme 3).

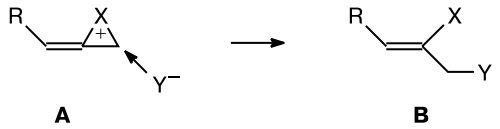
Scheme 3



This is indirect evidence for the fact that the MeO group can stabilize cationoid intermediates in the formation of diiodides from allenes **1**—**8**. The results of the experiment with enone **6** are also of importance. In this case, *Z*,*E*-diiodides **19** and **20** were obtained in equal amounts. It is difficult to say whether this is the result of the absence of stereoselectivity of the addition of I_2 at the double bond or an accidental equal percentage of two isomers due to the opposite effects of various factors (for example, subsequent isomerization cannot be excluded). Nevertheless, we attempted to analyze our results taking into account the known data.

According to the data published in the literature,[3,15,16] iodination of allenes in solutions in MeOH, CCl_4, or Py proceeds through intermediate iodonium cations **A**, which trap nucleophiles to give predominantly *Z*-alkenyl diiodides **B** (Scheme 4). Oxymercuration, bromination of allenes, *etc*. proceed analogously.[17,18]

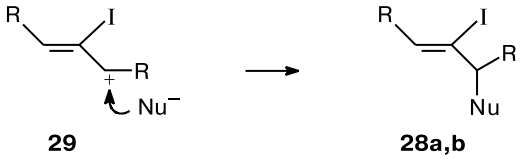
Scheme 4



However, in our experiments we observed the predominant formation of *E*-isomeric diiodides (compounds **9**, **11**, **15**, **21**, and **23**), whereas an excess of *Z* isomers (*E* : *Z* ≈ 4 : 6) was obtained for allenes **3** and **5**. The reaction of allene **1** with I_2 in MeOH afforded predominantly *E*-diiodide **9**. The possible MeO derivatives were not found.

In the literature,[3] the mechanism of the synthesis of *E*-dihalogen and halomethoxy derivatives (**28**) was described as the initial addition of I^+ to the central atom of allene followed by the capture of the external nucleophile (I^-, MeO^-) by cation **29**. In the case under consideration, the reactions cannot proceed according to this mechanism because the MeO group was not trapped and compound **28b** was not produced (Scheme 5).

Scheme 5

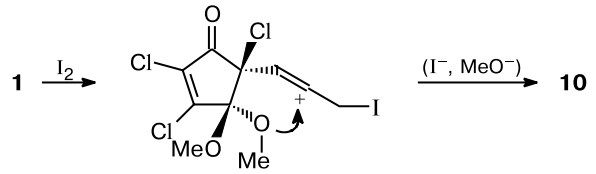


Nu = Hal (**28a**), OMe (**28b**)

Therefore, we assume another mechanism involving the formation of an alternative vinylic cationic intermediate (**30**)[3] in the course of iodination of allenes, for example, in the case of allene **1** (Scheme 6).

As can be seen from Scheme 6, cation **30** can be stabilized by the adjacent C(5)Cl and MeO groups due to which the randomized vinylic cation is blocked from the backside[19] and is subjected to the attack by the I^- ion from the front. In this case, the competitive capture of the MeO group does not occur because this would be in con-

Scheme 6



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tradiction with the principles of the theory of hard and soft acids and bases.[20]

We attribute an increase in the percentage of the *Z* isomer observed in iodination of allenes **3** and **5** to the inefficiency of the above-mentioned stabilization (as in cation **30**) and the fact that the reaction follows the known pathway **29** → **28**.

The result of iodination of C(5)-dechlorinated allenylcyclopentenone **6**, which indicates that the presence of the Cl atom at C(5) is of importance for stereoselective iodination, deserves comments. In this case, *E*- and *Z*-isomeric diiodides **19** and **20** were produced in equal amounts. Formally, it could be concluded that the addition of iodine proceeded nonstereoselectively. However, the steric effects of the H atom and the functionalized cyclopentenone substituent in monosubstituted allene are too large to ignore the steric control over the addition of I_2 at the double bond. Hence, it seems probable that iodination of allene **6** proceeds both through the cyclic iodonium cation and the vinylic cationic intermediate (partial stabilization by the MeO group) to give *Z*- and *E*-diiodides, respectively.

Therefore, based on the data on the ratios between the *Z*,*E*-isomeric diiodides derived from allenes **1**, **2**, **7**, and **8**, it can be concluded that the stereoselectivity of electrophilic iodination is influenced by the C(5)Cl and dimethoxy groups. In addition, the possibility of the predominant formation of *E*-diiodides from allenes is of considerable interest because these isomers are potential substrates for Sm^{II}-promoted intramolecular tandem cyclization—fragmentation reactions.[21,22]

Experimental

The IR spectra were recorded on UR-20 and Specord M-80 instruments (in a film or Nujol mulls). The ^1H and ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer (^1H, 300.13 MHz; ^{13}C, 75.47 MHz) in $CDCl_3$; the signals of the residual protons and the C atom of the solvent were used as the internal standard (^1H NMR, δ 7.27; ^{13}C NMR, the central signal at δ 77.00). The mass spectra were obtained on an MKh-1306 instrument; the energies of ionizing electrons were 20 and 70 eV; the temperature of the ionization chamber was 75—100 °C. The course of the reaction was monitored by TLC (Silufol, hexane—AcOEt); visualization was carried out using an alkaline solution of $KMnO_4$.[23]

(5*S*,*R*)-5-Allenyl-2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-one (1) was prepared in 78% yield according to a procedure described earlier.[4]

(1*S*,5*R*)-5-Allenyl-2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-ol (2). Sodium borohydride (1.04 g, 27.4 mmol) was added to a solution of ketone **1** (5.18 g, 18.3 mmol) in MeOH (50 mL) at 20 °C. The reaction mixture was stirred for 30 min and then a 3% HCl solution was added dropwise to pH 5. The solution was concentrated and the product was extracted with CH_2Cl_2 (3×20 mL). The combined organic extracts were washed with a saturated NaCl solution (2×15 mL), dried with $MgSO_4$, and concentrated. Alcohol **2** was isolated by column chromatography of the residue on SiO_2 (hexane—AcOEt, 7 : 3) in a yield of 4.05 g (97%) as a colorless oil, R_f 0.38 (hexane—AcOEt, 7 : 3). Found (%): C, 41.98; H, 3.82; Cl, 37.37. $C_{10}H_{11}Cl_3O_3$. Calculated (%): C, 42.06; H, 3.88; Cl, 37.25. IR, ν/cm^{-1}: 1625, 1960, 3500. ^1H NMR, δ: 2.65 (br.s, 1 H, OH); 3.38 and 3.39 (both s, 3 H each, 2×OMe); 4.16 (s, 1 H, CHO); 4.98 (d, 2 H, CH_2=C, J = 6.8 Hz); 5.60 (t, 1 H, =CH, J = 6.8 Hz). ^{13}C NMR, δ: 50.6 and 52.0 (OMe); 77.9 (C(1)); 79.0 (C(5)); 79.5 (C(3′)); 91.8 (C(1′)); 104.4 (C(4)); 130.9 (C(3)); 136.1 (C(2)); 208.2 (C(2′)).

(4*S*,5*R*)-5-Allenyl-2,3,5-trichloro-4-hydroxycyclopent-2-en-1-one (3). Concentrated HCl (5 mL) was added to a stirred solution of alcohol **2** (4.05 g, 14.10 mmol) in Me_2CO (80 mL) and then the reaction mixture was stirred for 4 h. After completion of the reaction (TLC control), the solution was concentrated and the residue was extracted with AcOEt. Combined organic extracts were washed with saturated Na_2CO_3 and NaCl solutions, dried with $MgSO_4$, and concentrated. Cyclopentenone **3** was isolated by column chromatography of the residue on SiO_2 (hexane—AcOEt, 8 : 2) in a yield of 3.22 g (95%) as a yellow oil, R_f 0.29 (hexane—AcOEt, 7 : 3). Found (%): C, 40.05; H, 2.19; Cl, 44.39. $C_8H_5Cl_3O_2$. Calculated (%): C, 40.12; H, 2.10; Cl, 44.41. IR, ν/cm^{-1}: 1752, 1952, 3500. ^1H NMR, δ: 3.88 (br.s, 1 H, OH); 4.97 (s, 1 H, CHO); 5.11 (d, 2 H, =CH_2, J = 6.6 Hz); 5.58 (t, 1 H, =CH, J = 6.6 Hz). ^{13}C NMR, δ: 69.4 (C(5)); 74.4 (C(4)); 81.2 (C(3′)); 90.0 (C(1′)); 130.5 (C(2)); 161.1 (C(3)); 188.0 (C(1)); 207.4 (C(2′)).

2-Allenyl-2,4,5-trichlorocyclopent-4-ene-1,3-diol (4) was prepared in 96% yield by reduction of hydroxy ketone **3** according to a procedure analogous to that described above for compound **2** as a colorless viscous oil, R_f 0.23 (hexane—AcOEt, 7 : 3). Found (%): C, 39.62; H, 3.33; Cl, 43.86. $C_8H_7Cl_3O_2$. Calculated (%): C, 39.78; H, 2.93; Cl, 44.03. IR, ν/cm^{-1}: 1752, 1952, 3480. ^1H NMR, δ: 3.17 (s, 2 H, OH); 4.55 (s, 2 H, CHO); 5.11 (d, 2 H, =CH_2, J = 6.7 Hz); 5.60 (t, 1 H, =CH, J = 6.7 Hz). ^{13}C NMR, δ: 78.4 (C(1) and C(4)); 80.6 (C(3′)); 80.7 (C(5)); 93.1 (C(1′)); 132.1 (C(2) and C(3)); 206.9 (C(2′)).

2-Allenyl-2,4,5-trichlorocyclopent-4-ene-1,3-dione (5). A solution of CrO_3 (0.3 g, 3 mmol) in a mixture of concentrated H_2SO_4 (0.6 mL) and H_2O (1.5 mL) was added dropwise with stirring to a solution of hydroxy ketone **3** (0.5 g, 2 mmol) in Me_2CO (10 mL) cooled to 0 °C. The reaction mixture was stirred at 0 °C for 2 h, heated to 20 °C, poured into ice water, and extracted with CH_2Cl_2 (3×30 mL). The extract was washed with a saturated NaCl solution and dried with $MgSO_4$. Then the solution was concentrated and the residue was chromatographed on SiO_2 (pentane—AcOEt, 7 : 3) to isolate dione **5** in a yield of 0.23 g (48%) as a viscous yellow oil, R_f 0.54 (hexane—AcOEt, 7 : 3). Found (%): C, 39.62; H, 3.33; Cl, 43.86. $C_8H_3Cl_3O_2$.

Calculated (%): C, 40.46; H, 1.27; Cl, 44.79. IR, ν/cm^{-1}: 1635, 1752, 1955. ^{1}H NMR, δ: 5.11 (d, 2 H, =CH_2 J = 6.5 Hz); 5.42 (t, 1 H, CH=, J = 6.5 Hz). ^{13}C NMR, δ: 61.1 (C(5)); 81.5 (C(3′)); 95.4 (C(1′)); 149.4 (C(2) and C(3)); 184.2 (C(1) and C(4)); 209.0 (C(2′)).

(5*S*,*R*)-5-Allenyl-2,3-dichloro-4,4-dimethoxycyclopent-2-en-1-one (6) was prepared in 58% yield according to a known procedure.[5]

(1*S*,5*R*)-5-Allenyl-2,3,5-trichloro-4,4-dimethoxy-1-(prop-2-ynyl)cyclopent-2-en-1-ol (7) was prepared in 87% yield according to a procedure published earlier.[6]

(1*S*,5*R*)-5-Allenyl-2,3,5-trichloro-1-ethynyl-4,4-dimethoxycyclopent-2-en-1-ol (8). A solution of allene **1** (2.0 g, 7.05 mmol) in anhydrous THF (5 mL) was added dropwise with stirring to a suspension of ethynylmagnesium bromide, which was prepared from Mg (0.4 g, 16.5 mmol) in anhydrous THF (12 mL), cooled with ice. The reaction mixture was stirred at 20 °C for 18 h and then a saturated NH_4Cl solution (10 mL) was added. The organic layer was separated and the aqueous layer was extracted with AcOEt. The organic extracts were combined, washed with water and a saturated NaCl solution, dried with $MgSO_4$, and concentrated. The residue was chromatographed on SiO_2 (hexane—AcOEt, 8 : 2) to isolate alcohol **8** in a yield of 1.73 g (79.3%) as a viscous colorless oil, R_f 0.33 (hexane—AcOEt, 8 : 2). Found (%): C, 46.35, H, 3.35, Cl, 34.88. $C_{12}H_{11}Cl_3O_3$. Calculated (%): C, 46.56, H, 3.58, Cl, 34.36. IR, ν/cm^{-1}: 1602, 1957, 2140, 3290, 3400. ^{1}H NMR, δ: 2.29 (t, 1 H, CH≡, J = 2.6 Hz); 2.85 (br.s, 1 H, OH); 3.43 and 3.53 (both s, 3 H each, 2×OMe); 4.98 (d, 2 H, =CH_2, J = 6.8 Hz); 5.6 (t, 1 H, =CH, J = 6.8 Hz). ^{13}C NMR, δ: 41.4 (C(1′′)); 50.9 and 52.0 (OMe); 78.8 (C(2′′)); 79.5 (C(3′)); 80.0 (C(5)); 80.0 (C(1)); 81.7 (C(1′)); 103.7 (C(4)); 133.0 (C(3)); 137.6 C(2)); 208.2 (C(2′)).

Reactions of compounds 1—8 with I_2 in CH_2Cl_2 (general procedure). A solution of I_2 (2.69 g, 1.06 mmol) in CH_2Cl_2 (70 mL) was added dropwise with stirring to a solution of substrate **1—8** (1.06 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred at 20 °C for 6 h, washed with saturated $Na_2S_2O_3$ and NaCl solutions, dried with $CaCl_2$, and concentrated. The residue was analyzed by ^{1}H NMR spectroscopy and then purified by column chromatography on SiO_2 (hexane—AcOEt, 7 : 3).

A mixture of diiodides **9** and **10** (E : Z = 86 : 14, ^{1}H NMR) was prepared in a total yield of 66%. Individual E isomer **9** was isolated by recrystallization from AcOEt, and Z-diiodide **10** was isolated by column chromatography on SiO_2 (light petroleum—AcOEt, 7 : 3).

(5*S*,*R*)-2,3,5-Trichloro-5-[(*E*)-2,3-diiodoprop-1-enyl]-4,4-dimethoxycyclopent-2-en-1-one (9). Compound **9** was prepared in a yield of 2.9 g (66%) as white crystals, m.p. 114—114.5 °C (AcOEt), R_f 0.47 (light petroleum—AcOEt, 7 : 3). Found (%): C, 22.50; H, 1.81; Cl, 19.68; I, 47.41. $C_{10}H_9Cl_3I_2O_3$. Calculated (%): C, 22.35; H, 1.69; Cl, 19.79; I, 47.23. IR, ν/cm^{-1}: 952, 1616, 1750. ^{1}H NMR, δ: 3.45 and 3.49 (both s, 3 H each, 2×OMe); 4.36 and 4.70 (both d, 1 H each, CH_2I, J = 10.7 Hz); 6.50 (s, 1 H, CH=). ^{13}C NMR, δ: 14.5 (CH_2I); 52.0 (OMe); 52.3 (OMe); 73.2 (C(5)); 101.7 (C(4)); 113.2 (C(2′)); 131.8 (C(1′)); 133.2 (C(2)); 157.1 (C(3)); 183.7 (C(1)).

(5*S*,*R*)-2,3,5-Trichloro-5-[(*Z*)-2,3-diiodoprop-1-enyl]-4,4-dimethoxycyclopent-2-en-1-one (10). Compound **10** was prepared in a yield of 0.52 g (10%) as a colorless oil, R_f 0.39 (light petroleum—AcOEt, 7 : 3). ^{1}H NMR, δ: 3.44 and 3.49 (both s, 3 H each, 2×OMe); 4.48 and 4.54 (both d, 1 H each, CH_2I, J = 10.5 Hz); 6.60 (s, 1 H, CH=). ^{13}C NMR, δ: 19.8 (CH_2I); 51.8 (OMe); 51.6 (OMe); 73.3 (C(5)); 102.9 (C(4)); 108.6 (C(2′)); 132.0 (C(1′)); 134.5 (C(2)); 156.2 (C(3)); 183.2 (C(1)).

A mixture of diiodides **11** and **12** (E : Z = 68 : 32, ^{1}H NMR) was prepared in a total yield of 60%. Individual isomers **11** and **12** were isolated by column chromatography on SiO_2 (light petroleum—AcOEt, 7 : 3).

(1*S*,5*R*)-2,3,5-Trichloro-5-[(*E*)-2,3-diiodoprop-1-enyl]-4,4-dimethoxycyclopent-2-en-1-ol (11). Colorless oil, R_f 0.29 (light petroleum—AcOEt, 7 : 3). Found (%): C, 22.39; H, 2.04; Cl, 19.60; I, 47.28. $C_{10}H_{11}Cl_3I_2O_3$. Calculated (%): C, 22.27; H, 2.06; Cl, 19.72; I, 47.06. IR, ν/cm^{-1}: 950, 1600, 3020, 3300. ^{1}H NMR, δ: 2.84 (d, 1 H, OH, J = 11.6 Hz); 3.43 and 3.46 (both s, 3 H each, 2×OMe); 4.58 (d, 1 H, CHO, J = 11.6 Hz); 4.69 and 4.71 (both d, 1 H each, CH_2I, J = 10.5 Hz); 6.82 (s, 1 H, CH=). ^{13}C NMR, δ: 14.4 (CH_2I); 50.8 (OMe); 52.3 (OMe); 77.4 (C(1)); 79.2 (C(5)); 104.4 (C(2′)); 108.4 (C(4)); 131.7 (C(3)); 135.5 (C(2)); 137.4 (C(1′)).

(1*S*,5*R*)-2,3,5-Trichloro-5-[(*Z*)-2,3-diiodoprop-1-enyl]-4,4-dimethoxycyclopent-2-en-1-ol (12). Colorless oil, R_f 0.19 (light petroleum—AcOEt, 7 : 3). IR, ν/cm^{-1}: 1650, 3020, 3300. ^{1}H NMR, δ: 2.90—3.10 (m, 1 H, OH); 3.43 and 3.46 (both s, 3 H each, 2×OMe); 4.38 (d, 1 H, CHO, J = 11.6 Hz); 4.52 and 4.58 (both d, 1 H each, CH_2I, J = 10.5 Hz), 6.69 (s, 1 H, CH=). ^{13}C NMR, δ: 19.9 (CH_2I); 51.6 (OMe); 51.8 (OMe); 77.6 (C(1)); 79.8 (C(5)); 104.5 (C(2′)); 108.7 (C(4)); 133.2 (C(3)); 133.4 (C(1′)); 136.6 (C(2)).

A mixture of diiodides **13** and **14** was prepared according to two procedures: (a) by iodination of allene **3** in a total yield of 50% (E : Z = 2 : 3, ^{1}H NMR) and (b) by acidic hydrolysis of a mixture of diiodides **11** and **12** (E : Z = 2 : 1, ^{1}H NMR) (according to a procedure analogous to that described for compound **3**) in a total yield of 77% (E : Z = 1 : 2, ^{1}H NMR). Individual isomers **13** and **14** were isolated by column chromatography on SiO_2 (light petroleum—AcOEt, 7 : 3).

(4*S*,5*R*)-2,3,5-Trichloro-5-[(*E*)-2,3-diiodoprop-1-enyl]-4-hydroxycyclopent-2-en-1-one (13). Colorless oil, R_f 0.24 (light petroleum—AcOEt, 7 : 3). Found (%): C, 19.33; H, 1.16; Cl, 21.71; I, 51.34. $C_8H_5Cl_3I_2O_2$. Calculated (%): C, 19.48; H, 1.02; Cl, 21.56; I, 51.45. IR, ν/cm^{-1}: 958, 1606, 1748, 3400. ^{1}H NMR, δ: 3.15 (s, 1 H, OH); 4.42 and 4.99 (both d, 1 H each, CH_2I, J = 10.7 Hz); 5.05 (s, 1 H, CHO); 6.67 (s, 1 H, CH=). ^{13}C NMR, δ: 13.9 (CH_2I); 68.5 (C(5)); 74.6 (C(4)); 112.2 (C(2′)); 132.0 (C(2)); 135.6 (C(1′)); 160.7 (C(3)); 186.3 (C(1)).

(4*S*,5*R*)-2,3,5-Trichloro-5-[(*Z*)-2,3-diiodoprop-1-enyl]-4-hydroxycyclopent-2-en-1-one (14). Colorless oil, R_f 0.15 (light petroleum—AcOEt, 7 : 3). IR, ν/cm^{-1}: 1615, 1746, 3020, 3300. ^{1}H NMR, δ: 3.13 (s, 1 H, OH); 4.42 and 4.50 (both d, 1 H each, CH_2I, J = 10.7 Hz); 5.16 (s, 1 H, CHO); 6.85 (s, 1 H, CH=). ^{13}C NMR, δ: 16.8 (CH_2I); 71.0 (C(5)); 74.3 (C(4)); 108.3 (C(2′)); 133.1 (C(2)); 135.4 (C(1′)); 160.7 (C(3)); 186.5 (C(1)).

A mixture of diiodides **15** and **16** (E : Z = 3 : 1, ^{1}H NMR) was prepared in a total yield of 58%. Individual isomers **15** and **16** were isolated by column chromatography on SiO_2 (light petroleum—AcOEt, 7 : 3).

2,3,5-Trichloro-2-[(*E*)-2,3-diiodoprop-1-enyl]cyclopent-4-ene-1,3-diol (15). Colorless oil, R_f 0.31 (light petroleum—AcOEt, 7 : 3). Found (%): C, 19.63; H, 1.36; Cl, 21.67; I, 51.01. $C_8H_7Cl_3I_2O_2$. Calculated (%): C, 19.41; H, 1.42; Cl, 21.47; I, 51.24. IR, ν/cm^{-1}: 958, 1606, 3400. ^{1}H NMR, δ: 2.92 (br.s, 2 H, OH); 4.59 (s, 2 H, CHO); 4.74 (s, 2 H, CH_2I); 6.56 (s, 1 H,

CH=). ^{13}C NMR, δ: 14.1 (CH_2I); 77.2 (C(1) and C(4)); 81.1 (C(5)); 109.4 (C(2′)); 131.0 (C(2) and C(3)); 139.0 (C(1′)).

2,4,5-Trichloro-2-[(*Z*)-2,3-diiodoprop-1-enyl]cyclopent-4-ene-1,3-diol (16). Colorless oil, R_f 0.23 (light petroleum—AcOEt, 7 : 3). IR, ν/cm^{-1}: 950, 1605, 3400. ^{1}H NMR, δ: 2.92 (s, 2 H, 2 OH); 4.47 (s, 2 H, CHO); 4.81 (s, 2 H, CH_2I); 6.48 (s, 1 H, CH=). ^{13}C NMR, δ: 18.6 (CH_2I); 76.4 (C(5)); 78.8 (C(1) and C(4)); 107.1 (C(2′)); 132.6 (C(2) and C(3)); 136.0 (C(1′)).

A mixture of diiodides **17** and **18** (*E* : *Z* = 35 : 65, ^{1}H NMR) was prepared in a total yield of 40%. Individual isomers **17** and **18** were isolated by column chromatography on SiO_2 (light petroleum—AcOEt, 7 : 3).

2,4,5-Trichloro-2-[(*E*)-2,3-diiodoprop-1-enyl]cyclopent-4-ene-1,3-dione (17). Colorless oil, R_f 0.62 (light petroleum—AcOEt, 7 : 3). Found (%): C, 19.39; H, 0.46; Cl, 21.76; I, 51.43. $C_8H_3Cl_3I_2O_2$. Calculated (%): C, 19.56; H, 0.62; Cl, 21.65; I, 51.66. IR, ν/cm^{-1}: 955, 1625, 1750. ^{1}H NMR, δ: 4.79 (s, 2 H, CH_2I); 6.19 (s, 1 H, CH=). ^{13}C NMR, δ: 13.1 (CH_2I); 60.8 (C(5)); 116.7 (C(2′)); 127.7 (C(1′)); 150.1 (C(2) and C(3)); 183.2 (C(1) and C(4)).

2,4,5-Trichloro-2-[(*Z*)-2,3-diiodoprop-1-enyl]cyclopent-4-ene-1,3-dione (18). Colorless oil, R_f 0.53 (light petroleum—AcOEt, 7 : 3). IR, ν/cm^{-1}: 1612, 1755. ^{1}H NMR, δ: 4.41 (s, 2 H, CH_2I); 6.86 (s, 1 H, CH=). ^{13}C NMR, δ: 15.4 (CH_2I); 62.1 (C(5)); 108.1 (C(2′)); 133.4 (C(1′)); 150.8 (C(2) and C(3)); 183.5 (C(1) and C(4)).

A mixture of diiodides **19** and **20** (*E* : *Z* = 1 : 1, ^{1}H NMR) was prepared in a total yield of 75%. Individual isomers **19** and **20** were isolated by column chromatography on SiO_2 (light petroleum—AcOEt, 7 : 3).

(5*S*,*R*)-2,3-Dichloro-5-[(*E*)-2,3-diiodoprop-1-enyl]-4,4-dimethoxycyclopent-2-en-1-one (19). Colorless oil, R_f 0.42 (light petroleum—AcOEt, 7 : 3). Found (%): C, 23.79; H, 2.23; Cl, 14.30; I, 50.29. $C_{10}H_{10}Cl_2I_2O_2$. Calculated (%): C, 23.88; H, 2.01; Cl, 14.11; I, 50.47. IR, ν/cm^{-1}: 948, 1610, 1745. ^{1}H NMR, δ: 3.35 and 3.42 (both s, 3 H each, 2×OMe); 3.63 (d, 1 H, C(5)H, *J* = 9.37 Hz); 4.02 and 4.62 (both d, 1 H each, CH_2I, *J* = 11.0 Hz); 8.62 (d, 1 H, CH=, *J* = 9.37 Hz). ^{13}C NMR, δ: 12.6 (CH_2I); 51.8 (OMe); 51.8 (OMe); 58.1 (C(5)); 102.1 (C(2′)); 108.7 (C(4)); 130.6 (C(1′)); 135.0 (C(2)); 158.2 (C(3)); 189.3 (C(1)).

(5*S*,*R*)-2,3-Dichloro-5-[(*Z*)-2,3-diiodoprop-1-enyl]-4,4-dimethoxycyclopent-2-en-1-one (20). Colorless oil, R_f 0.36 (light petroleum—AcOEt, 7 : 3). IR, ν/cm^{-1}: 1650, 1730. ^{1}H NMR, δ: 3.32 and 3.42 (both s, 3 H each, 2×OMe); 3.47 (d, 1 H, C(5)H, *J* = 8.8 Hz); 4.26 and 4.62 (both d, 1 H each, CH_2I, *J* = 11.0 Hz); 8.93 (d, 1 H, CH=, *J* = 8.8 Hz). ^{13}C NMR, δ: 17.4 (CH_2I); 51.6 (OMe); 51.8 (OMe); 65.4 (C(5)); 101.9 (C(2′)); 111.0 (C(4)); 133.4 (C(1′)); 135.0 (C(2)); 158.9 (C(3)); 188.4 (C(1)).

A mixture of diiodides **21** and **22** (*E* : *Z* = 9 : 1, ^{1}H NMR) was prepared in a total yield of 73%. Individual isomers **21** and **22** were isolated by column chromatography on SiO_2 (light petroleum—AcOEt, 7 : 3).

(1*S*,5*R*)-2,3,5-Trichloro-5-[(*E*)-2,3-diiodoprop-1-enyl]-4,4-dimethoxy-1-(prop-2-ynyl)cyclopent-2-en-1-ol (21). Colorless oil, R_f 0.28 (light petroleum—AcOEt, 7 : 3). Found (%): C, 26.91; H, 2.18; Cl, 18.58; I, 44.09. $C_{13}H_{13}Cl_3I_2O_3$. Calculated (%): C, 27.04; H, 2.27; Cl, 18.42; I, 43.96. IR, ν/cm^{-1}: 962, 1600, 1640, 2100, 3160, 3550. ^{1}H NMR, δ: 2.13 (t, 1 H, CH≡, *J* = 2.5 Hz); 2.70 (m, 2 H, CH_2); 3.30 and 3.40 (both s, 3 H each, 2×OMe); 4.35 and 5.08 (both dd, 1 H, CH_2I, *J* = 10.5 Hz, *J* = 4.2 Hz); 6.76 (d, 1 H, HC=, *J* = 4.2 Hz). ^{13}C NMR, δ: 15.7 (CH_2I); 26.8 (CH_2); 50.2 (OMe); 52.5 (OMe); 72.6 (≡CH); 78.2 (—C≡); 82.3 (C(5)); 83.4 (C(1)); 106.1 (C(4)); 110.5 (C(2′)); 130.5 (C(3)); 134.7 (C(1′)); 137.9 (C(2)).

(1*S*,5*R*)-2,3,5-Trichloro-5-[(*Z*)-2,3-diiodoprop-1-enyl]-4,4-dimethoxy-1-(prop-2-ynyl)cyclopent-2-en-1-ol (22). Colorless oil, R_f 0.21 (light petroleum—AcOEt, 7 : 3). IR, ν/cm^{-1}: 1600, 1640, 2100, 3160, 3550. ^{1}H NMR, δ: 2.10 (t, 1 H, ≡CH, *J* = 2.5 Hz); 2.68 (m, 2 H, CH_2); 3.33 and 3.43 (both s, 3 H each, 2×OMe); 4.40 and 4.62 (both d, 1 H each, CH_2I, *J* = 10.5 Hz); 6.98 (s, 1 H, CH=). ^{13}C NMR, δ: 21.9 (CH_2I); 29.6 (CH_2); 50.3 (OMe); 52.4 (OMe); 78.2 (—C≡); 79.6 (≡C); 81.9 (C(5)); 82.9 (C(1)); 106.5 (C(2′)); 130.3 (C(3)); 131.4 (C(1′)); 139.0 (C(2)).

A mixture of diiodides **23** and **24** (*E* : *Z* = 84 : 16, ^{1}H NMR) was prepared in a yield of 88%. Individual isomers **23** and **24** were isolated by column chromatography on SiO_2 (light petroleum—AcOEt, 7 : 3).

(1*S*,5*R*)-2,3,5-Trichloro-5-[(*E*)-2,3-diiodoprop-1-enyl]-1-ethynyl-4,4-dimethoxycyclopent-2-en-1-ol (23). Colorless oil, R_f 0.3 (light petroleum—AcOEt, 7 : 3). Found (%): C, 25.91; H, 2.18; Cl, 18.58; I, 44.69. $C_{12}H_{11}Cl_3I_2O_3$. Calculated (%): C, 25.57; H, 1.96; Cl, 18.87; I, 45.07. IR, ν/cm^{-1}: 960, 1600, 1740, 2100, 3301, 3550. ^{1}H NMR, δ: 2.03 (s, 1 H, CH≡); 3.52 and 3.54 (both s, 3 H each, 2×OMe); 4.55 and 5.68 (both d, 1 H each, CH_2I, *J* = 10.5 Hz); 6.83 (s, 1 H, HC=). ^{13}C NMR, δ: 16.7 (CH_2I); 51.4 (OMe); 53.4 (OMe); 71.6 (≡CH); 77.7 (—C≡); 79.7 (C(5)); 82.9 (C(1)); 105.2 (C(4)); 108.9 (C(2′)); 129.2 (C(3)); 134.2 (C(1′)); 138.9 (C(2)).

(1*S*,5*R*)-2,3,5-Trichloro-5-[(*Z*)-2,3-diiodoprop-1-enyl]-1-ethynyl-4,4-dimethoxycyclopent-2-en-1-ol (24). Colorless oil, R_f 0.21 (light petroleum—AcOEt, 7 : 3). IR, ν/cm^{-1}: 1600, 1740, 2105, 3301, 3550. ^{1}H NMR, δ: 2.10 (s, 1 H, CH≡); 3.53 and 3.54 (both s, 3 H each, 2×OMe); 4.40 and 4.62 (both d, 1 H each, CH_2I, *J* = 10.5 Hz); 6.98 (s, 1 H, CH=). ^{13}C NMR, δ: 20.2 (CH_2I); 51.3 (OMe); 52.5 (OMe); 75.1 (≡CH), 79.5 (—C≡); 80.3 (C(5)); 82.3 (C(1)); 104.9 (C(4)); 107.1 (C(2′)); 130.1 (C(3)); 130.4 (C(1′)); 139.3 (C(2)).

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