(±)-2,3,5-Trichloro-4,4-ethylenedioxycyclopent-2-en-1-one and its 5-allyl-substituted derivative in conjugated 1,4-addition with dimethyldilithium cyanocuprate

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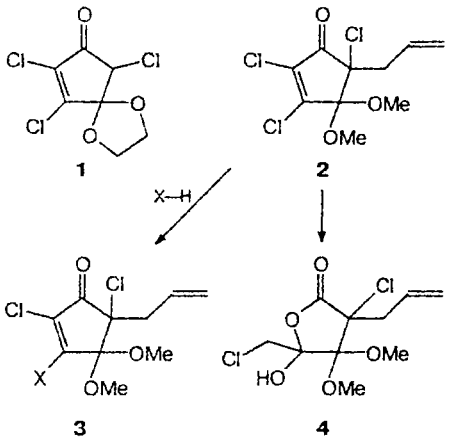
(±)-2,3,5-Trichloro-4,4-ethylenedioxycyclopent-2-en-1-one reacts with $Me_2CuCNLi_2$ to give depending on conditions the corresponding 3-methyl substituted cyclopentenone (Ad_NE adduct) or a mixture of unsaturated acyclic acids formed as the result of abnormal cleavage reaction of C(1)—C(2) bond in the trichorocyclopentenone. Reactions of conjugated 1,4-addition of $Me_2CuCNLi_2$ to (±)-5-allyl-2,3,5-trichloto-4,4-dimethoxycyclopent-2-en-1-one lead to products of replacement of vinylic Cl atom at C(3) by Me group and those of C(5)-dechlorination.

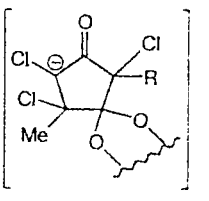
Key words: trichlorocyclopentenones, cuprate reagents, conjugated 1,4-addition.

Trichlorocyclopentenones **1** and **2** originally synthesized by us[1,2] contain the enone system and the ketal function at the C(4) atom activated by the two Cl atoms, and Cl atom at the C(5) atom. They are of interest as unique multireactive acceptors in Michael conjugated 1,4-addition of various nucleophiles, especially, "cuprate reagents".[3] Little is known about the behavior of these systems toward nucleophilic agents. The most studied compound in this respect is trichlorocyclopentenone **2**, from which the C(3)-heterosubstituted products (**3**),[4] the 1,2-adducts at the carbonyl group in reactions with Grignard reagents,[5,6] and lactone **4**, which was formed by keeping **2** in a Bu^tONa—Bu^tOH system,[7] have been previously obtained. Similar reactions of trichlorocyclopentenone **1** have not been studied.



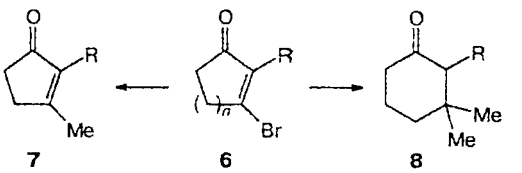
(X = NR^1R^2, SR, OR etc.)

Cuprate reagents can be characterized as "mild C-nucleophiles" that react with enones according to the scheme of conjugated 1,4-addition. In this work a comparative study of reactions of dimethyldilithium cyanocuprate with substrates **1** and **2** has been carried out in order to determine the possibility of generation of "primary" enolates **5** and to find out whether they are relatively stable (the Cl atom at the C(2) atom exerts a stabilizing effect on the carbanion) and suitable for *in situ* alkylation with electrophiles or they are subjected to side processes of fragmentation and intramolecular rearrangements. The reaction of an excess of lithium dimethylcuprate with β-bromocyclopentenone or β-bromocyclohexenone (**6**) afforded β-methylcyclopentenone (**7**) and 3,3-dimethylcyclohexenones (**8**), respectively.[8]



5

(R = H, All)



(*n* = 1, 2; R = Alk)

A transformation similar to the **6** → **7** reaction affording 4-hydroxysubstituted analog of **7** is described in Ref. 9.

It is known that in reactions of N-, O-, and S-nucleophiles with compound **2** the intermediate carban-

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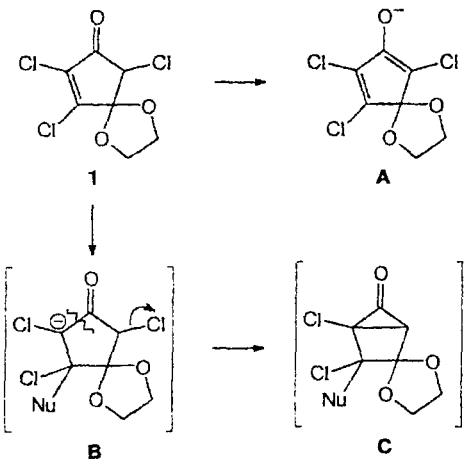
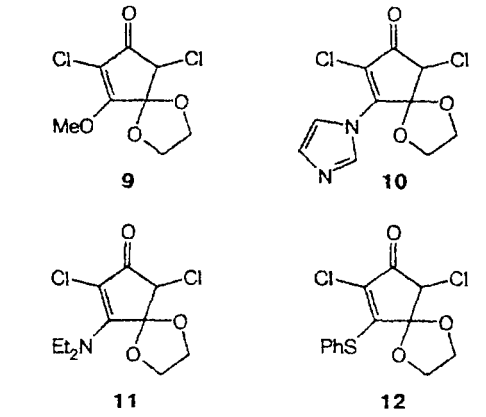
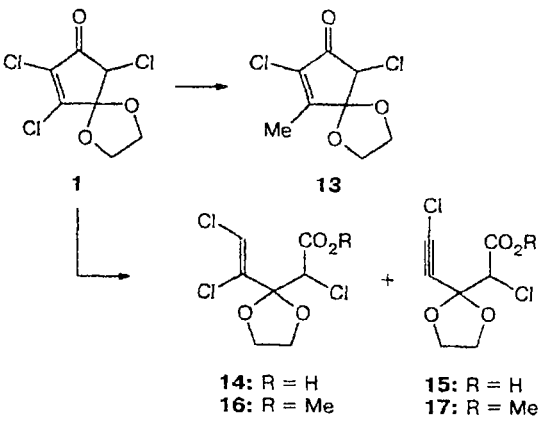
ion, which is similar to intermediate **5**, is stabilized by detachment of Cl atom from the C(3) atom to give compound **3** (the Ad_NE-mechanism).[4] Since the formally similar trichlorocyclopentenones **1** and **2** differ significantly by their C(5) centers (the mobile H atom is present in the structure **1**), for the reactions of compound **1** with nucleophiles in basic media, the pathway of conjugated 1,4-addition may be blocked as the result of enolization with the formation of oxanion **A***; even if the expected carbanion **B** is generated, its behavior is unpredictable. Anion **B** may be stabilized according to both the Ad_NE-mechanism mentioned for compound **2** and by other means, *i.e.*, by fragmentation with the cleavage of the C(1)—C(2) bond or through the Favorskii type intermediate **C**, the precursor of the corresponding products of cycle diminution.



Therefore, we decided to begin with the studies of some typical reactions of enone **1** with the simplest heteronucleophiles. It turned out that the reactions of enone **1** with MeONa in MeOH, imidazole, and Et_2NH in benzene, and PhSNa in MeOH, similar to the **2** → **3** transition, proceed without complications and afford compounds **9**—**12** in high yields. The common feature of all the studied reactions is a strictly regioselective substitution of Cl atom at the C(3) atom: even the hard nucleophile MeONa in MeOH does not cause ring cleavage in the cyclopentenone **1**. At the same time, enone **2** under similar conditions (Bu^tONa—Bu^tOH) gives compound **4**.

When we became aware that trichlorocyclopentenone **1** reacts with heteronucleophiles to form the expected products, we began a study of its reactions with dimethyldilithium cyanocuprate.[10] The reaction of enone **1** with 2.5 equiv. of $Me_2Cu(CN)Li_2$ was carried out in Et_2O at −78 °C until the starting compound was completely consumed (TLC, ~1 h). After work up of the reaction mixture and purification of the residue on SiO_2, 3-methylcyclopentenone (**13**) was isolated as a main product; however, the formation of more polar minor compounds was also noted. Monitoring of the reaction by TLC indicated that these components appear primarily on the step of the standard work up of the reaction mixture (NH_4Cl—H_2O, 20 °C, 30 min). The repeated experiment that involved mixing of the reagents in the same ratio at −78 °C, rapid (~5 min) increase in temperature to −20 °C, and treatment of the reaction mixture with a NH_4Cl—H_2O mixture followed by stirring at 20 °C for 30 min allowed us to isolate a mixture of the two main acyclic acids (**14** and **15**) in 60% yield, which were identified as methyl esters **16** and **17**. It is noteworthy that keeping mixtures of ethereal solution of compound **1** with aqueous solutions of LiOH—CuCN and LiOH—NH_4Cl invariably afforded complex mixtures of difficultly separable compounds. Thus, though we were not able to model the side process, it is nevertheless clear that cuprate reagent participates in the opening of the cycle in **1** (initiates the reaction).

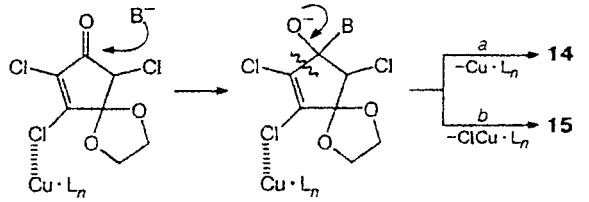




A possible mechanism of the formation of the acyclic acids from enone **1** includes the primary coordination of the Cu-reagent not at the double bond of **1** (no transfer of the Me group!) but with the most mobile Cl atom at

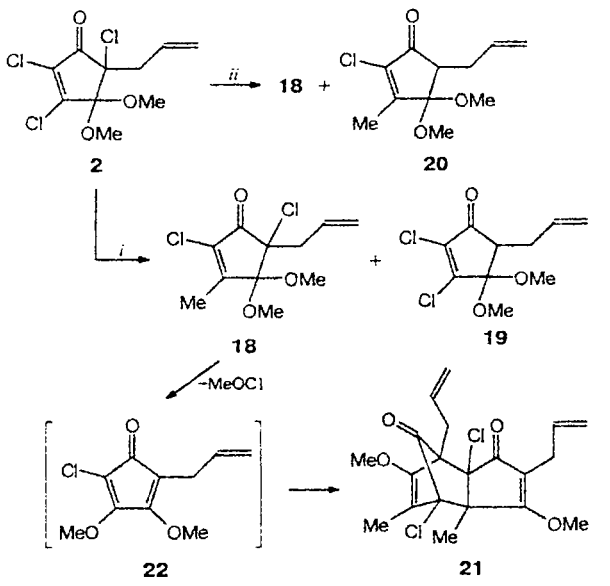
*Upon treatment of **1** with MeLi (Et_2O, −10 °C) the reaction mixture turns deep red; however, the color disappears and the unreacted starting compound is recovered after acidifying the mixture.

the C(3) atom. This favors an additional activation of the carbonyl group, which leads to the possibility of its attack by nucleophiles present in the reaction medium (OH^-, Cl^-, or CN^-) and the formation of the intermediate anion **D**. This anion is further stabilized by transformation into products **14** and **15** (paths *a* and *b*).



D

At the next step, under the conditions similar to those used for the reaction of **1** with the cuprate, 2.5 equiv. of $Me_2Cu(CN)Li_2$ were taken for the reaction with enone **2** to afford compounds **18** and **19** in a 7 : 1 ratio in 50% yield. The reaction proceeds extremely rapidly (5 min, −60 °C). The product of reductive dechlorination (**19**) is apparently formed according to the mechanism of the "enolization promoted" detachment of Cl^- from the C(5) atom of compound **2**. An increase in the amount of the cuprate reagent used in the reaction to 4 equiv. results in the formation of compounds **18** and **20** (in a 6 : 4 ratio) in a total yield up to 95%; possible products of further addition of cuprate (derivatives of compounds **18** and **20**, 3,3-dimethylcyclopentanones) were not found in the reaction mixtures. It is interesting to note that a slow non-catalyzed formation of diketone **21** is observed on storage of purified samples of **18**. The former is obviously formed from the highly reactive cyclopentadienone **22** generated from **18** by homolytic cleavage of MeOCl. In addition to the molecular ion, the mass spectrum of **21** contains an intense peak corresponding to the ion of its retrodiene component **22**.



i. 2.5 equiv. $Me_2Cu(CN)Li_2$, −60 °C, 5 min
ii. 4 equiv. $Me_2Cu(CN)Li_2$, −60 °C

Thus, the results obtained allow us to conclude that trichlorocyclopentenones **1** and **2** are good acceptors of nucleophiles in the Michael reaction. They react with $Me_2CuCNLi_2$ according to the Ad_NE-mechanism; however, the results of the reactions of **1** with nucleophilic agents may be ambiguous due to the formation of side acyclic products.

Experimental

IR spectra were obtained on an UR-20 spectrophotometer in thin layers or as suspensions in nujol. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrophotometer (300 (^1H) and 75.47 MHz (^{13}C)) in $CDCl_3$ with $SiMe_4$ as the internal standard. Mass spectra were recorded on a MX-1306 instrument with ionizing voltage 70 eV and temperature of the ionizing chamber 75—100 °C.

(±)-1,3-Dichloro-4-methoxy-6,9-dioxaspiro[4.4]non-3-en-2-one (9). A solution of ketone **1** (2 g) and MeONa (0.43 g) in MeOH (10 mL) was refluxed for 3 h. The solvent was evaporated, the residue was dissolved in H_2O (15 mL), and the product was extracted with AcOEt (3×20 mL). The combined organic extracts were dried with $MgSO_4$, filtered off, and concentrated. The oily residue was purified by column chromatography on SiO_2 to give 1.62 g (62%) of compound **9**. Found (%): C, 39.88; H, 3.17; Cl, 29.95. $C_8H_8O_4Cl_2$. Calculated (%): C, 40.19; H, 3.37; Cl, 29.66. IR (ν/cm^{-1}): 1630, 1745. ^1H NMR, δ: 4.15—4.30 (m, 4 H, 2 CH_2); 4.36 (s, 3 H, OMe); 4.52 (s, 1 H, CH). ^{13}C NMR, δ: 60.27 (C-1); 61.22 (Me); 106.69 (C-5); 109.60 (C-3); 170.84 (C-4); 187.09 (C-2).

(±)-2,4-Dichloro-1-*N*-imidazolyl-6,9-dioxaspiro[4.4]non-1-en-3-one (10). A solution of ketone **1** (2 g) and imidazole (1.2 g) in benzene (10 mL) was refluxed for 3 h. The solvent was evaporated, the residue was dissolved in H_2O (15 mL), and the product was extracted with AcOEt (3×20 mL). The combined organic extracts were dried with $MgSO_4$ and concentrated. The residue was crystallized from AcOEt to give 1.36 g (86%) of compound **10**, m.p. 130—131 °C. Found (%): C, 43.60; H, 2.92; Cl, 25.60; N, 10.30. $C_{10}H_8Cl_2N_2O_3$. Calculated (%): C, 43.63; H, 2.90; Cl, 25.81; N, 10.18. IR (ν/cm^{-1}): 730, 835, 1020, 1060, 1130, 1210, 1760, 3140, 3170. ^1H NMR, δ: 4.15—4.42 (m, 4 H, 2 CH_2O); 4.60 (s, 1 H, CHCl); 7.17 (s, 1 H, CH); 7.54 (s, 1 H, CH); 8.08 (s, 1 H, CH=). ^{13}C NMR, δ: 61.70 (C-5); 66.39 and 66.62 (CH_2O); 108.0 (C-4); 118.08 (CH=N); 123.49 (C-3); 130.62 (C-4); 136.89 (C-5); 149.23 (C-2); 186.80 (C=O).

(±)-2,4-Dichloro-1-(*N*,*N*-diethylamino)-6,9-dioxaspiro[4.4]non-1-en-3-one (11). Et_2NH (0.72 g) was added to a solution of ketone **1** (1 g) in benzene (10 mL), and the reaction mixture was stirred at ~20 °C for 24 h. The solvent was evaporated, H_2O was added, and the mixture was extracted with CH_2Cl_2 (3×50 mL). The combined extracts were dried with $MgSO_4$, the solvent was evaporated, and the product was purified by column chromatography on SiO_2 (pentane—AcOEt, 1 : 1) to give 0.93 g (81%) of compound **11**. Found (%): C, 47.20; H, 5.30; Cl, 25.40; N, 4.95. $C_{11}H_{15}Cl_2NO_3$. Calculated

(%): C, 47.14; H, 5.35; Cl, 25.35; N, 5.00. IR (ν/cm^{-1}): 1480, 1600, 1710, 1740, 3070. ^{1}H NMR, δ: 1.20 (t, 6 H, 2 CH_3, J = 7 Hz); 3.40—3.70 (m, 4 H, 2 CH_2); 4.10—4.40 (m, 5 H, CH, 2 CH_2O). ^{13}C NMR, δ: 14.52 (CH_3); 45.52 (CH_2); 62.70 (C-4); 66.87 and 66.44 (2 OCH_2); 103.50 (C-1); 108.94 (C-5); 157.20 (C-2); 183.89 (C-3).

(±)-2,4-Dichloro-1-phenylthio-6,9-dioxaspiro[4.4]non-1-en-3-one (12). Thiophenol (0.136 g) and ketone **1** (0.3 g) were added with stirring to a solution of MeONa prepared from Na (0.0283 g) and dry MeOH (5 mL). The reaction mixture was stirred for 0.5 h, H_2O was added, and the product was extracted with CH_2Cl_2 (3×20 mL). The combined organic extracts were washed with a saturated aqueous NaCl solution until neutral reaction and dried with $MgSO_4$, and the residue was concentrated to give 0.37 g of raw product that was purified by column chromatography on SiO_2 (pentane—AcOEt, 2 : 1) to give 0.28 g (72%) of oily compound **12**. Found (%): C, 49.15; H, 3.23; Cl, 22.50. $C_{13}H_{10}Cl_2O_3S$. Calculated (%): C, 49.21; H, 3.15; Cl, 22.39. IR (ν/cm^{-1}): 1516, 1616, 1736, 3096. ^{1}H NMR, δ: 3.45—3.58 (m, 2 H, 2 CH_2O); 3.95—4.15 (m, 2 H, CH_2O); 4.48 (s, 1 H, C(5)H); 7.35—7.65 (m, 5 H, 5 CH_{Ar}). ^{13}C NMR, δ: 62.89 (C-4); 66.44 and 66.61 (CH_2O); 109.83 (C-5); 129.06 (C-2,6); 130.13 (C-4); 130.51 (C-1); 135.85 (C-3,5); 163.18 (C-2); 186.05 (C-3).

Reaction of trichlorocyclopentenone 1 with dimethyldilithium cyanocuprate. *A.* A solution of enone **1** (0.6 g, 1.7 mmol) in THF (3 mL) was added to a solution of $Me_2(CN)CuLi_2$ prepared from CuCN (0.28 g, 3.02 mmol) and MeLi (12 mL, 6.4 mmol, 0.57 *N* in Et_2O) in THF (5 mL) at −78 °C with stirring in an argon atmosphere. The reaction mixture was kept at −78 °C for 1 h, treated with an aqueous NH_4Cl solution, extracted with CH_2Cl_2 (3×20 mL), dried with $MgSO_4$, and concentrated, and the residue was purified by column chromatography on SiO_2 (pentane—AcOEt, 1 : 1) to give 0.3 g (45%) of compound **13**.

(±)-2,4-Dichloro-1-methyl-6,9-dioxaspiro[4.4]non-1-en-3-one (13). Found (%): C, 42.83; H, 3.48; Cl, 32.07. $C_8H_8O_3Cl_2$. Calculated (%): C, 43.08; H, 3.62; Cl, 31.79. IR (ν/cm^{-1}): 1644, 1664, 1720. ^{1}H NMR, δ: 2.05 (s, 3 H, CH_3); 4.10—4.30 (m, 4 H, 2 CH_2O); 4.65 (s, 1 H, CHCl). ^{13}C NMR, δ: 11.36 (CH_3); 64.62 (C-4); 67.40 and 68.00 (2 CH_2O); 110.77 (C-5); 134.11 (C-2); 165.74 (C-1); 196.33 (C-3).

B. A solution of MeLi (37 mL, 10.6 mmol, 0.57 *N* in Et_2O) was added at 0 °C in an Ar atmosphere to a solution of CuCN (0.46 g, 5.2 mmol) in THF (5 mL), the mixture was cooled to −78 °C, and a solution of trichlorocyclopentenone **1** (1 g, 4.77 mmol) in THF (5 mL) was added. The temperature was increased to −20 °C in 5 min, the reaction mixture was treated with an aqueous NH_4Cl solution, stirred at 20 °C for 30 min, and extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were dried with $MgSO_4$, the solution was concentrated, and the product was purified by column chromatography on SiO_2 (pentane—AcOEt, 1 : 1) to give a mixture of acids **14** and **15** in a 3 : 2 ratio in 60% total yield. Acid **14** was isolated in an individual form by repeated chromatography of the mixture on SiO_2. The spectral characteristics of acid **14** were obtained for its mixture with a decreased content of **13** after methylation of this mixture with CH_2N_2.

(±)-(*Z*)-2,4,5-Trichloro-3,3-ethylenedioxypent-4-enoic acid (14). IR (ν/cm^{-1}): 1620, 1680, 1740, 3088, 3600. ^{1}H NMR, δ: 4.82 (s, 1 H, C-2); 6.79 (s, 1 H, C(5)H); 10.12 (br.s, CO_2H). ^{13}C NMR, δ: 57.42 (C-2); 66.52 and 66.76 (OCH_2CH_2O); 107.34 (C-3); 121.33 (C-5); 131.39 (C-4); 169.0 (C-1).

(±)-2,5-Dichloro-3,3-ethylenedioxypent-4-ynoic acid (15). IR (ν/cm^{-1}): 1740, 2220, 3600. ^{1}H NMR, δ: 3.90—4.20 (m, 4 H, 2 CH_2O); 4.32 (s, 1 H, C(2)H); 10.12 (br.s, CO_2H). ^{13}C NMR, δ: 59.76 (C-2); 63.78 (C-5); 66.63 (C-4); 66.11 and 66.45 (OCH_2CH_2O), 101.13 (C-3); 169.0 (C-1).

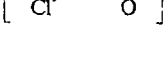
Methyl (±)-(*Z*)-2,4,5-trichloro-3,3-ethylenedioxypent-4-enoate (16) was obtained in quantitative yield upon treatment of acid **14** with a small excess of a CH_2N_2 solution in Et_2O. Ester **16** was purified by chromatography. Found (%): C, 35.12; H, 3.24; Cl, 38.93. $C_8H_9O_4Cl_3$. Calculated (%): C, 34.87; H, 3.30; Cl, 38.60. IR (ν/cm^{-1}): 1608, 1756, 3088. ^{1}H NMR, δ: 3.80 (s, 3 H, OCH_3); 4.05 and 4.20 (both m, 4 H, 2 CH_2O); 4.87 (s, 1 H, C(2)H); 6.88 (s, 1 H, C(5)H). ^{13}C NMR, δ: 53.35 (OCH_3); 57.69 (C-2); 66.38 and 66.87 (OCH_2CH_2O); 107.80 (C-3); 121.43 (C-5); 131.92 (C-4); 166.34 (C-1). MS, *m/z*: 274 $[M]^+$, 259 $[M-CH_3]^+$, 239 $[M-Cl]^+$, 209 $[M-Cl-CH_2O]^+$, 203 $[M-Cl-HCl]^+$, 167 $[M']^{+*}$, 131 $[M'-HCl]^+$, 123 $[M'-C_2HO]^+$, 107 $[ClCH-CO_2Me]^+$.

Methyl (±)-2,4,5-trichloro-3,3-ethylenedioxypent-4-ynoate (17) was obtained by a similar procedure. IR (ν/cm^{-1}): 1756, 2224. ^{1}H NMR, δ: 3.75 (s, 3 H, OCH_3); 4.00—4.10 (m, 4 H, 2 CH_2O); 4.37 (s, 1 H, C(2)H). ^{13}C NMR, δ: 53.04 (OCH_3); 59.79 (C-2); 63.95 (C-5); 66.03 (OCH_2CH_2O); 66.20 (C-4); 101.27 (C-3); 165.77 (C-1). MS, *m/z*: 238 $[M]^+$, 223 $[M-Me]^+$, 203 $[M-Cl]^+$, 131 $[M-Cl-CH_2OMe]^+$.

Reaction of trichlorocyclopentenone 2 with dimethyldilithium cyanocuprate. A solution of enone **2** (0.5 g, 1.7 mmol) in THF (5 mL) was added dropwise with stirring at −60 °C to a solution of $Me_2(CN)CuLi_2$, prepared from CuCN (0.32 g, 3.5 mmol) and MeLi (4.4 mL, 7.0 mmol, 1.6 mol L^{-1} in Et_2O), in THF (5 mL). The reaction mixture was kept at this temperature for 5 min and then poured into a mixture of NH_4Cl—NH_4OH (9 : 1) (20 mL). The solution was extracted with ether (3×10 mL), dried with $MgSO_4$, and concentrated, and the residue was purified by column chromatography on SiO_2 (pentane—ether, 9 : 1) to give 0.22 g (44%) of compound **18** and 0.03 g (6%) of enone **19**. The reaction of **2** with 4 equiv. of $Me_2CuCNLi_2$ under similar conditions afforded compounds **18** and **20** in a 6 : 4 ratio in 95% total yield.

(±)-5-Allyl-2,5-trichloro-3-methyl-4,4-dimethoxycyclopent-2-en-1-one (18). Found (%): C, 49.67; H, 5.30; Cl, 26.55. $C_{11}H_{14}Cl_2O_3$. Calculated (%): C, 49.81; H, 5.28; Cl, 26.79. IR (ν/cm^{-1}): 1740, 1650 (—CH=C=O). ^{1}H NMR, δ: 2.15 (s, 3 H, CH_3); 2.37 (m, 1 H, CH_2); 2.57 (t, 1 H, CH_2); 3.28 (s, 3 H, OCH_3); 3.34 (s, 3 H, OCH_3); 4.95—5.10 (m, 2 H, CH_2=); 5.84—5.98 (m, 1 H, —CH=). ^{13}C NMR, δ: 13.72 (CH_3); 30.78 (OCH_2); 51.18 (OCH_3); 53.91 (OCH_3); 77.3 (C-5); 104 (C-4); 116.32 (CH_2=); 134.0 (C-2); 136.0 (=CH); 163.78 (C-3); 196.89 (C-1). MS, *m/z*: 230 $[M]^+$, 215 $[M-CH_3]^+$, 199 $[M-OCH_3]^+$, 198 $[M-CH_3OH]^+$, 195 $[M-Cl]^+$.

(±)-5-Allyl-2,3-dichloro-4,4-dimethoxycyclopent-2-en-1-one (19). Found (%): C, 47.65; H, 4.78; Cl, 28.28. $C_{10}H_{12}Cl_2O_3$. Calculated (%): C, 47.80; H, 4.78; Cl, 28.28. IR (ν/cm^{-1}): 1740, 1650, 1620. ^{1}H NMR, δ: 2.47—2.52 (m, 1 H, CH_2); 2.84 (t, 1 H, CH_2, J = 6.5 Hz); 3.41 (s, 3 H, OCH_3); 3.57 (s, 3 H, OCH_3); 5.08—5.18 (m, 2 H, CH_2); 5.90—5.98 (m, 1 H, CH). ^{13}C NMR, δ: 30.75 (CH_2); 51.65 (OCH_3); 51.83 (C-5); 55.38 (2 OCH_3); 102.66 (C-4); 117.21 (CH_2=); 131.43 (C-2); 135.51 (CH=); 158.32 (C-3); 194.14 (C-1).

** $[M']^+ = [M-ClCHCO_2Me]^+$ = 

(±)-5-Allyl-2-chloro-4,4-dimethoxy-3-methylcyclopent-2-en-1-one (20). Found (%): C, 57.03; H, 6.48; Cl, 15.60. $C_{11}H_{15}ClO_3$. Calculated (%): C, 57.26; H, 6.50; Cl, 15.40. IR (ν/cm^{-1}): 1740, 1650, (—CH=C—C=O). ^1H NMR, δ: 2.12 (s, 3 H, CH_3); 2.37 (t, 2 H, CH_2, J = 6.5 Hz); 2.56 (t, 1 H, C(5)H, J = 6.5 Hz); 3.26 (s, 3 H, OCH_3); 3.32 (s, 3 H, OCH_3); 4.94—5.05 (m, 2 H, CH_2=); 5.82—5.96 (m, 1 H, CH=). ^{13}C NMR, δ: 13.76 (CH_3); 30.82 (CH_2); 51.24 (2 OCH_3); 53.94 (C-5); 104.16 (C-4); 116.38 (CH_2=); 134.03 (C-2); 136.05 (CH=); 163.78 (C-3); 196.91 (C-1).

(±)-1,4-Diallyl-2,7-dichloro-5,9-dimethoxy-6,8-dimethyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3,10-dione (21) is slowly formed from enone **18** on storage in refrigerator (~20% in 3 months), m.p. 34—34.5 °C. IR (ν/cm^{-1}): 1800 (C=O); 1690, 1615, (=C—C=O), 1650, 1620 (C=C). ^1H NMR, δ: 1.32 (s, 3 H, C-6, CH_3); 1.82 (s, 3 H, C-8, CH_3); 2.57—2.60 (m, 2 H, CH_2); 3.15—3.20 (m, 2 H, CH_2); 3.81 (s, 3 H, C-8, OCH_3); 4.13 (s, 3 H, C-5, OCH_3); 5.00—5.22 (m, 2 H, 2 CH=); 5.76 (m, 4 H, 2 CH_2=). ^{13}C NMR, δ: 10.89 (q, C-2, CH_3); 16.81 (q, C-9, CH_3); 27.03 and 27.10 (t, 2 CH_2); 53.99 (s, C-2); 59.42 and 60.05 (q, 2 OCH_2); 60.05 (s, C-6); 73.60 (s, C-1); 76.96 (s, C-7); 109.04 (s, C-4); 115.78 and 118.41 (t, 2 H_2C=); 118.06 (s, C-8); 133.04 and 135.85 (d, 2 CH=); 153.12 (s, C-9); 181.57 (s, C-4); 191.40 (s, C-5); 194.32 (s, C-10). MS, *m/z*: 396 $[M]^+$, 368 $[M-CO]^+$, 361 $[M-Cl]^+$, 198 $[M/2]^+$.

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