(*cf.* Ref. 6: m.p. 210—212 °C). Found (%): C, 22.7; H, 4.2; I, 26.5; N, 3.0; Si, 5.6; Te, 26.7. $C_9H_{20}INO_3SiTe$. Calculated (%): C, 22.9; H, 4.3; I, 26.8; N, 3.0; Si, 5.9; Te, 27.0. ^1H NMR (CD_3OD), δ: 2.18 (s, 6 H, $(CH_3)_2Te^+$); 1.81 (s, 2 H, $SiCH_2$); 3.00 (t, 6 H, NCH_2); 3.81 (t, 6 H, OCH_2).

B. A mixture of telluronium iodide **7** (1.4 g, 2.5 mmol) and MeI (2 mL) was refluxed for 1 h. The reaction mixture was cooled and pentane (20 mL) was added. The precipitate that formed was filtered off, washed with pentane and dried *in vacuo* to give telluronium iodide **9** (0.9 g, 81%), m.p. 209—211 °C (from MeOH).

Dimethyl silatranylmethyl selenonium iodide (10). Selenide **5** (2.55 g, 5 mmol) was refluxed in MeI (5 mL) for 3 h. The reaction mixture was cooled to −20 °C and diluted with pentane (30 mL). The precipitate that formed was filtered off, washed with pentane and dried *in vacuo* to give iodide **10** (1.8 g, 85%), m.p. 173—174 °C (from MeOH) (*cf.* Ref. 4: m.p. 178—180 °C). Found (%): C, 25.3; H, 4.7; I, 30.2; N, 3.4; Se, 18.3; Si, 6.7. $C_9H_{20}INO_3SeSi$. Calculated (%): C, 25.5; H, 4.8; I, 29.9; N, 3.3; Se, 18.6; Si, 6.6. ^1H NMR (CD_3OD), δ: 2.13 (s, 2 H, $SiCH_2$); 2.65 (s, 9 H, CH_3Se^+); 3.03 (t, 6 H, NCH_2); 3.83 (t, 6 H, OCH_2). Phenylethynyl iodide was identified by GLC in the filtrate after concentration.

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Recyclization of 5-allenyl-2,5-dichloro-3-*N*,*N*-dimethylamino-4,4-dimethoxycyclopent-2-enone under the action of SmI_2—$(Me_2N)_3P$. Functionalized *cis*-,*trans*-cycloocta-2,6-dienones

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Reaction of 5-allenyl-2,5-dichloro-3-*N*,*N*-dimethylamino-4,4-dimethoxycyclopent-2-enone with SmI_2—$(Me_2N)_3P$ affords new functionalized *cis*-,*trans*-cycloocta-2,6-dienones.

Key words: allenylcyclopentenones, samarium diiodide, hexamethylphosphorous triamide, recyclization, functionalized *cis*-,*trans*-cycloocta-2,6-dienones.

Earlier,[1] we found that SmI_2, a one-electron reductive agent, which is widely used in organic synthesis,[2] is transformed in the presence of $(Me_2N)_3P$ into more reactive SmI intermediates (supposedly, Me_2NSmI). The latter generate ketyl-radicals from cyclopentenone (**1**), which undergoes a series of cascade transformations resulting in a tropone derivative. Note that compound **1** and a related compound (**2**)[3] are inert[4,5] with respect to SmI_2—$(Me_2N)_3PO$—THF under standard conditions. In the present work, we studied the reaction of allenyl-

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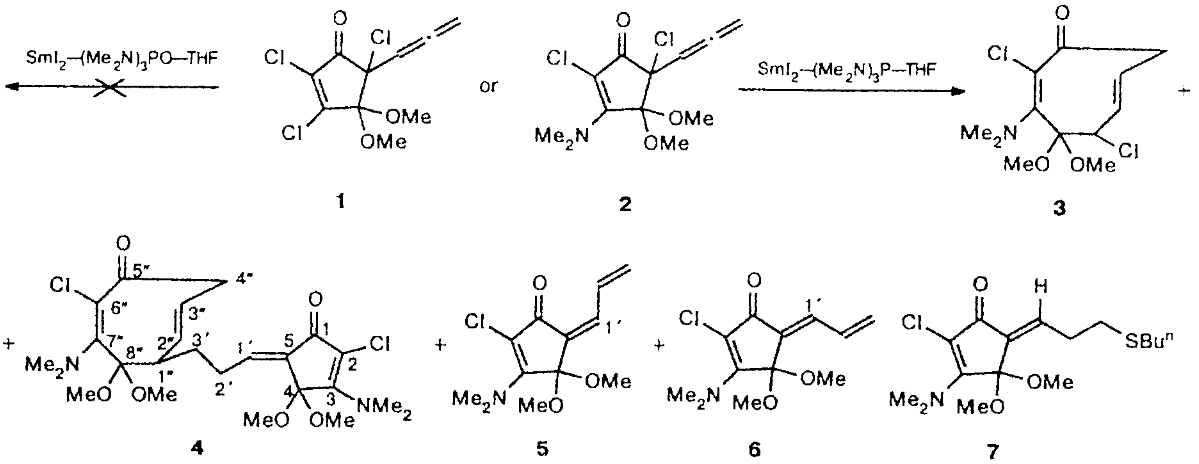
Scheme 1



cyclopentenone **2** with an SmI_2—$(Me_2N)_3P$—THF reagent. It was shown that compound **2** is rapidly transformed into a mixture of products (**3**—**6**) in overall yield >80% under conditions described for **1**,[1] the ratio **3** : **4** : **5** : **6** being equal to 38 : 33 : 10 : 19 (Scheme 1).

In the transformation studied, attention should be paid, first of all, to the formation of sterically hindered *Z,E*-cyclooctadienones **3** and **4**. The (*E*)-configuration of their disubstituted double bonds follows from ^{1}H NMR spectroscopic data (J = 15.2 Hz) (*cf.* Refs. 6 and 7). The (*E*)-configuration of the exocyclic double bond in compound **4** was ascribed with consideration of the ^{1}H NMR spectroscopic data for cyclopentenone (**7**) and its (*Z*)-isomer.[8] In these compounds, the chemical shift of a triplet signal for the vinylic proton is characteristic: being shielded by the carbonyl group in compound **7**, it is shifted downfield ($\delta_{C=CH}$ 6.66) compared to the corresponding signal for the *Z*-isomer ($\delta_{C=CH}$ 6.05). For comparison, the resonance frequency of the HC(1′) signal in compound **4** is equal to δ 6.68. Similarly, in the case of isomeric trienones **5** and **6**, the HC(1′) signal for the former is shifted upfield compared to the latter.

Experimental

IR spectra were recorded on UR-20 and Specord-80 spectrometers (thin film or suspension in Nujol). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300 and 75 MHz, respectively) in $CDCl_3$ with Me_4Si as the internal standard. Mass spectra were measured on an MKh-1320 instrument (ionizing voltage 70 eV, ionizing chamber temperature 50—70 °C).

Reaction of 5-allenyl-2,5-dichloro-3-*N,N*-dimethylamino-4,4-dimethoxycyclopent-2-enone with the SmI_2—$(Me_2N)_3P$—THF reagent. A suspension of samarium (1.44 g, 9.6 mg-at.) in 30 mL of dry THF was vigorously stirred in an atmosphere of argon, and CH_2I_2 (2.33 g, 8.7 mmol) was rapidly added. The reaction mixture was stirred at ~20 °C for 2 h (the suspension turned blue-green), and then $(Me_2N)_3P$ (6.72 g, 41.2 mmol) was added. The resulting purple solution was stirred at ~20 °C for 30 min, cooled to 0 °C, and then a solution of compound **2** (0.5 g, 1.7 mmol) in 70 mL of dry THF was added over 2 h. The reaction mixture was heated to ~20 °C and stirred for an additional 45 min. The course of the reaction was monitored by TLC (Silufol, ethyl acetate). After the reaction was completed (TLC), a saturated aqueous solution of $NaHCO_3$ was added to the reaction mixture, and the products were extracted with CH_2Cl_2. The combined organic extracts were washed with water and a saturated solution of NaCl, dried with $MgSO_4$, and concentrated. The reaction products were isolated by column chromatography on SiO_2 (benzene—ethyl acetate, 1 : 1).

2,5-Dichloro-3-dimethylamino-4,4-dimethoxycycloocta-2*Z*,6*E*-dienone (3). M.p. 124—126 °C (ethyl acetate). Found (%): C, 49.13; H, 5.68; Cl, 23.18; N, 5.10. $C_{12}H_{17}Cl_2NO_3$. Calculated (%): C, 48.99; H, 5.83; Cl, 24.10; N, 4.76. IR, ν/cm^{-1}: 980, 1592, 1688. ^{1}H NMR, δ: 2.12 (dd, 1 H, H(8^A), J_1 = 12.3 Hz, J_2 = 3.1 Hz); 2.18 (dd, 1 H, H(8^B), J_1 = 12.3 Hz, J_2 = 3.0 Hz); 3.21 (d, 1 H, H(5), J = 8.6 Hz); 3.27 and 3.29 (both s, 6 H, 2 OMe); 3.35 (s, 6 H, NMe_2); 5.33 (dd, 1 H, H(6), J_1 = 15.2 Hz, J_2 = 8.6 Hz); 5.79 (ddd, 1 H, H(7), J_1 = 15.2 Hz, J_2 = 3.1 Hz, J_3 = 3.0 Hz). ^{13}C NMR, δ: 32.30 (C(8)); 41.66 (NMe_2); 51.36 (OMe); 51.74 (OMe); 54.96 (C(5)); 103.14 (C(4)); 105.98 (C(2)); 123.23 (C(7)); 135.61 (C(6)); 160.82 (C(3)); 190.90 (C(1)). MS, *m/z*: 258 [M − HCl]$^+$ (max).

2-Chloro-3-dimethylamino-4,4-dimethoxy-5-[(*E*)-3-(6-chloro-7-dimethylamino-8,8-dimethoxy-5-oxocycloocta-(2*E*,6*Z*)-dienyl)propylidene]cyclopent-2-enone (4). Found (%): C, 55.55; H, 6.79; Cl, 13.46; N, 5.25. $C_{24}H_{34}N_2Cl_2O_6$. Calculated (%): C, 55.71; H, 6.62; Cl, 13.70; N, 5.41. IR, ν/cm^{-1}: 980, 1610, 1710. ^{1}H NMR, δ: 1.52 (dt, 2 H, H(3′), J_1 = 7.6 Hz, J_2 = 7.6 Hz, J_3 = 6.8 Hz); 2.12 (dt, 1 H, H(1″), J_1 = 8.6 Hz, J_2 = J_3 = 6.8 Hz); 2.15 (d, 2 H, H(4″), J = 5.9 Hz); 2.40 (dt, 2 H, H(2′), J_1 = 7.8 Hz, J_2 = J_3 = 7.6 Hz); 3.16 (s, 6 H, 2 OMe); 3.26 and 3.29 (both s, 6 H, 2 OMe); 3.34 (s, 6 H, NMe_2); 3.36 (br.s, 6 H, NMe_2); 5.37 (dd, 1 H, H(2″), J_1 = 15.2 Hz, J_2 = 8.6 Hz); 5.79 (dt, 1 H, H(3″), J_1 = 15.2 Hz, J_2 = 5.9 Hz); 6.68 (t, 1 H, H(1′), J = 7.6 Hz). ^{13}C NMR, δ: 26.97 (C(3′)); 27.98 (C(2′)); 32.59 (C(4″)); 41.50 (NMe); 41.67 (NMe); 51.38 (OMe); 51.76 (OMe); 51.84 (2 OMe); 55.03 (C(1″)); 103.25 (C(8″)); 105.93 (C(4)); 106.72 (C(2)); 107.50 (C(6″)); 123.41 (C(3″));

128.73 (C(5)); 135.26 (C(1′)); 135.69 (C(2″)); 158.10 (C(7″)); 160.79 (C(3)); 182.45 (C(1)); 190.89 (C(5″)).

2-Chloro-3-dimethylamino-4,4-dimethoxy-(5*Z*)-(prop-2-enylidene)cyclopent-2-enone (5). Found (%): C, 55.72; H, 6.08; Cl, 13.48; N, 5.61. $C_{12}H_{16}ClNO_3$. Calculated (%): C, 55.93; H, 6.25; Cl, 13.76; N, 5.43. IR, ν/cm^{-1}: 1600, 1725. ^{1}H NMR, δ: 3.18 (s, 6 H, 2 OMe); 3.43 (s, 6 H, NMe_2); 5.53 (dd, 1 H, $=CH_2$, J_1 = 10 Hz, J_2 = 1 Hz); 5.58 (m, 1 H, $=CH_2$); 6.36 (d, 1 H, $CH_2=CH-C\underline{H}=$, J = 11 Hz); 7.04 (ddd, 1 H, $CH_2C\underline{H}-CH=$, J_1 = 17 Hz, J_2 = 11 Hz, J_3 = 10 Hz). ^{13}C NMR, δ: 41.54 (NMe_2); 51.85 (2 OMe); 105.38 (C(4)); 109.50 (C(2)); 126.11 ($=CH_2$); 127.90 (C(5)); 132.15 and 132.20 ($=CH-CH=$); 157.54 (C(3)); 182.98 (C(1)). MS, *m/z*: 257 $[M]^+$, 242 $[M - Me]^+$, 226 $[M - MeO]^+$, 222 $[M - Cl]^+$.

2-Chloro-3-dimethylamino-4,4-dimethoxy-(5*E*)-(prop-2-enylidene)cyclopent-2-enone (6). Found (%): C, 56.19; H, 6.02; Cl, 13.51; N, 5.28. $C_{12}H_{16}ClNO_3$. Calculated (%): C, 55.93; H, 6.25; Cl, 13.76; N, 5.43. IR, ν/cm^{-1}: 1600, 1725. ^{1}H NMR, δ: 3.13 (s, 6 H, 2 OMe); 3.43 (s, 6 H, NMe_2); 5.55 (dd, 1 H, $=CH_2$, J_1 = 10.2 Hz, J_2 = 1.5 Hz); 5.63 (dd, 1 H, $=CH_2$, J_1 = 16.8 Hz, J_2 = 1.5 Hz); 6.90 (ddd, 1 H, $CH_2=C\underline{H}-CH=$, J_1 = 16.8 Hz, J_2 = 11.8 Hz, J_3 = 10 Hz); 7.05 (d, 1 H, $CH_2=CH-C\underline{H}=$, J = 11.8 Hz). ^{13}C NMR, δ: 41.68 (NMe_2); 51.88 (2 OMe); 106.56 (C(4)); 108.37 (C(2)); 127.26 ($=CH_2$); 128.22 (C(5)); 130.07 ($CH_2=\underline{C}H$); 131.02 ($CH_2=CH-\underline{C}H=$); 158.20 (C(3)); 182.61 (C(1)).

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P^{III}-Derivatives of methyl mercaptoacetate

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Dichlorophenylphosphine and dichlorodiethylamidophosphite react with methyl (trimethylsilylthio)acetate to substitute the methoxycarbonylmethylthio group for one Cl atom.

Key words: dichlorophenylphosphine, dichlorodiethylamidophosphite, methyl (trimethylsilylthio)acetate, chloridophosphothioites.

Earlier,[1] we have shown that the reaction of $RPCl_2$ (or PCl_3) with α-mercapto ketones in the presence of a base is accompanied by cyclization involving the carbonyl group. P^{III}-Derivatives of alkyl mercaptoacetates exhibit interesting chemical properties. Refluxing of a mixture of equimolar amounts of PCl_3 and alkyl mercaptoacetates in benzene yields alkoxycarbonylmethylphosphorodichloridothioites, which, when heated to 180—190 °C, cyclize into 2-chloro-5-oxo-1,3,2-oxathiaphospholane. Alkoxycarbonylmethylphosphorothioites and -phosphoramidites synthesized on their basis easily undergo[2] thiophosphite-thiophosphonate isomerization under the action of oxygen at room temperature.

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