Interaction of dimethylsulfoxonium methylide with 5-allyl-2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-one

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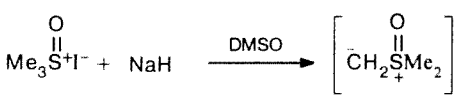
Dimethylsulfoxonium methylide in DMSO initiates unusual oxidative skeletal transformations of trichlorocyclopentenone. Lactone, cyclic orthoester, and a number of by-products of hydrolysis, substitution, and reduction were isolated and characterized. The expected epoxide was obtained in low yield.

Key words: 5-allyl-2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-one, dimethylsulfoxonium methylide.

Dimethylsulfoxonium methylide (**1**)[1] reacts with aldehydes and ketones to give epoxides,[2–4] cyclopropanates α,β-unsaturated carbonyl compounds smoothly,[5,6] diolefinates acetylenes containing electron-withdrawing groups,[7] undergoes deprotonation under the action of strong bases with the formation of hyperactivated ylides,[8,9] reacts with α,β-unsaturated β-chloroenones to give the corresponding allyl ylides,[10,11] and enters into other reactions.[12]

As part of continuing studies of the properties and the synthetic applications of a new trichlorocyclopentenone (**2**),[13–16] in this work we report the results of studies of the reaction of **2** with ylide **1** generated *in situ* from trimethylsulfoxonium iodide according to Scheme 1.

Scheme 1

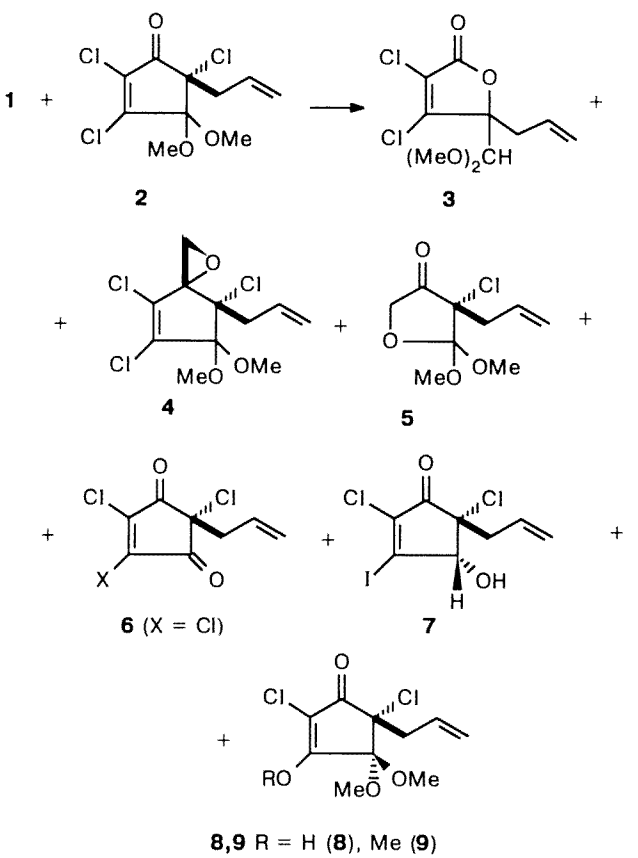


1

Cyclopentenone **2** is a multiply substituted multicenter reactant prone to unusual transformations.[17] In the reaction with ylide **1**, compound **2** acts as a "chemical chameleon" to form, depending on the reaction conditions, the diverse compounds (**3**—**8**) shown in Scheme 2.

For example, the reaction of equimolar amounts of **1** and **2** in DMSO distilled over KOH and then over CaH_2 (20 °C, 1 h) proceeded selectively to form α,β-unsaturated lactone **3**. However, conversion of **2** was no more than 30%. Conversion of **2** increased to 40% as the reaction time increased (20 °C, 36 h). In this case, compounds **3** and **4** were obtained in the ratio of 4 : 1. According to the spectral data, epoxide **4** is stereochemically homogeneous. The α configuration of the epoxide ring was accepted taking into account the fact that the direction of the nucleophilic attack at the keto group of compound **2** is sterically controlled exclusively by the Cl atom at the C(5) atom.[18,19] The reaction of

Scheme 2



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equimolar amounts of compounds **1** with **2** at 60 °C for 6 h was accompanied by substantial resinification of the reaction mixture. Chromatographic separation gave lactone **3** (25%), orthoester **5** (15%), and an unidentified compound (as a mixture with **3**). When less anhydrous DMSO, which had been distilled over powdered KOH, was used in this reaction (20 °C, 24 h), several products also formed. In addition to lactone **3** and orthoester **5** characterized previously, diketone **6** (5%), iodoalcohol **7** (8%), and enol **8** were isolated (conversion of **2** was 60%). The structure of enol **8** was established by converting **8** into the known enol ether **9** [20] by treatment with CH_2N_2. Apparently, the products of the hydrolysis of compound **2** form due to the presence of NaI, which is eliminated at the stage of ylide generation and of traces of water and I_2, which initiate hydrolytic cleavage of the dimethyl ketal group (direct acid hydrolysis of **2** gives diketone **6** in low yield[21]) and of the sp^2-hybridized C(3)—C(1) center (compound **8**).

Apparently, iodoalcohol **7** [21] forms from the extremely reactive diketone **6** through the replacement of one Cl atom by an I atom according to Finkelstein followed by the reduction of the keto group in the intermediate compound **6** (X = I) (unconsumed ylide or NaH is the source of hydride ions).

On the whole, it can be stated that the reaction of ylide **1** with trichlorocyclopentenone **2** gives the desired epoxide **4** only in low yield. The mechanistic aspects of the formation of unusual compounds **3** and **5** with substantial rearrangement of the skeleton of **2** and the changes in the degree of oxidation of particular carbon atoms remain obscure and call for additional studies.

Experimental

The IR spectra were recorded on an UR-20 spectrophotometer in thin films. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AM-300 spectrometer operating at 300 and 75.47 MHz, respectively; Me_4Si was used as the internal standard; $CDCl_3$ was used as the solvent. The mass spectra were measured on an MKh-1306 instrument; the ionizing voltage was 70 eV; the temperature of the ionization chamber was 75—100 °C.

Reaction of dimethylsulfoxonium methylide 1 with cyclopentenone 2. ***A.*** A solution of enone **2** (0.5 g) in DMSO (5 mL) (distilled over KOH and then over CaH_2) was added with stirring to a solution of ylide **1** prepared from a solution of NaH (0.07 g) and $[Me_3S^+O]I^-$ (0.42 g) in DMSO (10 mL) under an Ar atmosphere. The reaction mixture was stirred at room temperature for 1 h. Then water (15 mL) was added, and the mixture was extracted with ether. The combined extracts were washed with water, dried with $MgSO_4$, and concentrated. Chromatography of the residue on a column packed with SiO_2 (a 7 : 3 pentane—ethyl acetate mixture was used as the eluent) gave the initial enone **2** and **(±)-4-allyl-2,3-dichloro-4-dimethoxymethyl-2-butenolide (3)** in yields of 0.035 g (conversion of **2** was 30%) and 0.06 g (45%), respectively. IR of compound **3**, ν/cm^{-1}: 1640, 1690, 1836. ^1H NMR ($CDCl_3$), δ: 2.60—2.85 (m, 2 H, CH_2); 3.30 (s, 3 H, OCH_3); 3.38 (s, 3 H, OCH_3); 5.10—5.20 (m, 2 H, $CH=C\underline{H}_2$); 5.80 (s, 1 H, OCHO); 5.82—5.95 (m, 1 H, $C\underline{H}=CH_2$). ^{13}C NMR ($CDCl_3$), δ: 39.03 (t, CH_2); 51.19 (q, OCH_3); 51.27 (q, OCH_3); 70.92 (s, C(4)); 100.46 (d, OCHO); 101.93 (s, C(2)); 144.97 (s, C(3)), 166.95 (s, C(1)). Mass spectrum, *m/z*: 266 $[M]^+$, 231 $[M-Cl]^+$, 235 $[M-CH_3O]^+$, 196 $[M-2\ Cl]^+$, 59 $[OCOMe]^+$.

B. The reaction mixture, which had been obtained under the conditions described above, was kept at 20 °C for 36 h. Subsequent standard workup and chromatographic separation gave compound **3** (0.03 g), **4** (0.02 g) (the total yield was 52%, the **3** : **4** ratio was 4 : 1), and enone **2** (0.3 g) (conversion of **2** was 40%).

(±)-4α-Allyl-4,6,7-trichloro-5,5-dimethoxy-1β-oxaspiro[2,4]hept-6-ene (4). In the IR spectrum, the typical absorption band of the carbonyl group is absent. ^1H NMR ($CDCl_3$), δ: 2.73 (d, 2 H, CH_2, J = 7 Hz); 3.12 (d, 1 H, CH_2O, J = 4.6 Hz); 3.22 (d, 1 H, CH_2O, J = 4.6 Hz); 3.46 (s, 3 H, OCH_3); 3.55 (s, 3 H, OCH_3); 5.10—5.20 (m, 2 H, $CH=C\underline{H}_2$); 5.72—5.90 (m, 1 H, $C\underline{H}=CH_2$). ^{13}C NMR ($CDCl_3$), δ: 39.94 (t, CH_2); 50.07 (t, C(2)); 51.74 and 52.12 (both q, 2 OCH_3); 69.30 (s, C(4)); 76.17 (s, C(3)); 119.30 (t, C(6)); 132.47 (d, C(7)).

C. The reaction mixture, which was obtained according to ***A***, was stirred at 60 °C for 6 h. Subsequent standard workup gave **2** (0.11 g, conversion of **2** was 78%), **3** (0.09 g, 25%), and **(±)-4-allyl-4-chloro-5,5-dimethoxytetrahydrofuran-3-one (5)** (0.04 g, 15%). IR of compound **5**, ν/cm^{-1}: 1770. ^1H NMR ($CDCl_3$), δ: 2.80 (m, 1 H, CH_2); 3.00 (m, 1 H, CH_2); 3.36 (s, 3 H, OCH_3); 3.66 (s, 3 H, OCH_3); 4.62 (d, 1 H, CH_2O, J = 8.8 Hz); 4.95 (d, 1 H, CH_2O, J = 8.8 Hz); 5.10—5.20 (m, 2 H, $CH=C\underline{H}_2$); 6.00 (m, 1 H, $C\underline{H}=CH_2$). ^{13}C NMR ($CDCl_3$), δ: 37.05 (t, CH_2); 53.59 and 55.23 (both q, 2 OCH_3); 71.44 (t, C(5)); 98.47 (s, C(3)); 119.81 (t, $CH=CH_2$); 131.66 (d, $CH=CH_2$); 164.29 (s, C(2)); 195.14 (s, C(4)). Mass spectrum, *m/z*: 220 $[M]^+$, 185 $[M-Cl]^+$, 127 (max).

D. When the reaction was carried out in DMSO distilled over KOH, compounds **3**, **5**, **6**, **7**, and **8** were obtaind in yields of 0.16 g (28%), 0.05 g (10%), 0.3 g (5%), 0.05 g (7%), and 0.05 g (10%), respectively.

(±)-2-Allyl-2,4,5-trichlorocyclopent-4-ene-1,3-dione (6). IR, ν/cm^{-1}: 1590, 1630, 1750. ^1H NMR ($CDCl_3$), δ: 2.85 (d, 2 H, CH_2, J = 7.4 Hz); 5.05—5.10 (m, 2 H, $CH=C\underline{H}_2$); 5.40—5.50 (m, 1 H, $C\underline{H}=CH_2$). ^{13}C NMR ($CDCl_3$), δ: 38.94 (t, CH_2); 61.15 (s, C(2)); 123.22 (t, $CH=CH_2$); 127.76 (d, $CH=CH_2$); 150.52 (s, C(4)); 186.33 (s, C(1) and C(3)).

(±)-5α-Allyl-2,5-dichloro-4β-hydroxy-3-iodocyclopent-2-enone (7). IR, ν/cm^{-1}: 1620, 1740, 3430. ^1H NMR ($CDCl_3$), δ: 2.75—2.95 (m, 2 H, CH_2); 4.75 (s, 1 H, CH); 5.15—5.30 (m, 1 H, $C\underline{H}=CH_2$); 5.25—5.35 (m, 2 H, $CH=C\underline{H}_2$). ^{13}C NMR ($CDCl_3$), δ: 40.62 (t, CH_2); 71.46 (s, C(5)); 73.66 (d, C(4)); 120.10 (t, $CH=CH_2$); 129.95 (d, $CH=CH_2$); 131.72 (s, C(2)); 161.64 (s, C(3)); 189.17 (s, C(1)). Mass spectrum, *m/z*: 332 $[M]^+$, 297 $[M-Cl]^+$, 205 $[M-I]^+$.

(±)-5-Allyl-2,5-dichloro-3-hydroxy-4,4-dimethoxycyclopent-2-enone (8). IR, ν/cm^{-1}: 1660, 1740, 3600. ^1H NMR ($CDCl_3$), δ: 2.90 (m, 2 H, CH_2); 5.10—5.20 (m, 2 H, $CH=CH_2$), 5.35—5.50 (m, 1 H, $CH=CH_2$); 9.70 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 38.97 (t, CH_2); 61.88 (s, C(2)); 122.36 (t, $CH=CH_2$); 126.72 (s, C(5)); 128.72 (d, $CH=CH_2$); 163.70 (s, C(4)); 188.18 (s, C(1)); 189.57 (s, C(3)). Mass spectrum, *m/z*: 220 $[M]^+$, 205 $[M-CH_3]^+$, 185 $[M-Cl]^+$.

(±)-5-Allyl-2,5-dichloro-3,4,4-trimethoxycyclopent-2-enone (9). A solution of enol **8** (0.05 g) in ether (3 mL) was treated with an etheral solution of CH_2N_2 until a yellow color persisted. After 0.5 h, the solvent was evaporated, and compound **9** was obtained in a yield of 0.05 g (96%). IR, ν/cm^{-1}: 1610, 1650, 1760. ^1H NMR ($CDCl_3$), δ: 2.85—2.95 (m, 2 H,

CH_2); 4.46 (s, OCH_3); 5.15—5.30 (m, 2 H, $CH{=}CH_2$). ^{13}C NMR ($CDCl_3$), δ: 39.09 (t, CH_2); 60.92 (q, OCH_3); 62.33 (s, C(2)); 122.53 (t, $CH{=}CH_2$); 128.61 (d, $CH{=}CH_2$); 129.62 (s, C(5)); 158.93 (s, C(3)); 162.77 (s, C(4)); 186.59 (s, C(1)).

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