Synthesis of (±)-2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-one

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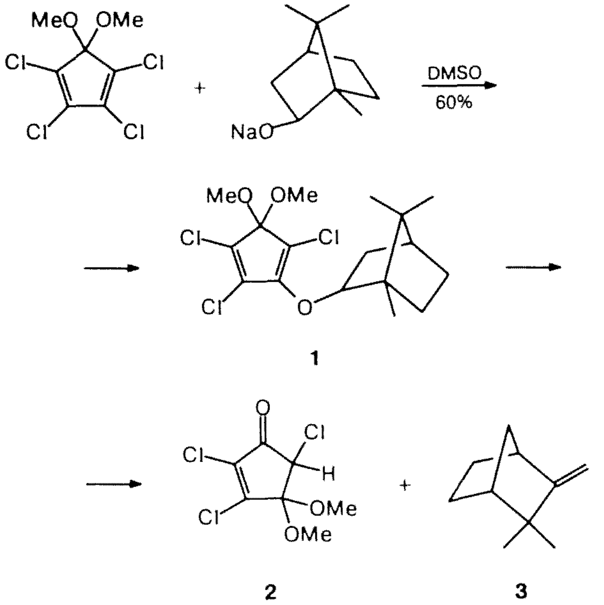
At 20 °C, (±)-1,3,4-trichloro-2-isobornyloxy-5,5-dimethoxycyclopentadiene slowly decomposes to give (±)-2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-one.

Key words: tetrachloro-5,5-dimetoxycyclopentadiene, reaction with isoborneol.

We found that the sodium alkoxide derived from racemic isoborneol reacts smoothly with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene[1] in DMSO to give vinyl ether (**1**). When the latter compound is kept at 20 °C for a month, it completely cleaves to afford trichlorocyclopentenone (**2**) and camphene (**3**). The overall yield of **2** is 48%.

The mechanism suggested for the spontaneous cleavage of compound **1** includes the intramolecular [1,6]-sigmatropic shift of a proton of the methyl group at the C-2 atom of the isobornyl fragment to the diene moiety of the molecule and reorganization of bonds in the transition state (**4**).



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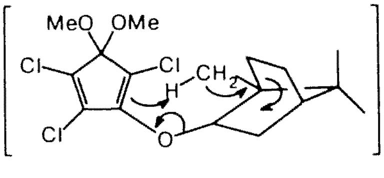

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Experimental

IR spectra were recorded on a UR-20 spectrophotometer as a suspension in Nujol. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-300 spectrometer operating at 300.13 and 75.47 MHz, respectively, using tetramethylsilane as the internal standard and $CDCl_3$ as the solvent. Mass spectra were recorded on an MX-1306 instrument at an ionizing voltage of 70 eV and at a temperature in the ionization chamber of 50—100 °C.

(±)-1,3,4-Trichloro-2-isobornyloxy-5,5-dimethoxycyclopentadiene (1). A solution of isoborneol (2 g, 13 mmol) in 5 mL of DMSO was added dropwise with stirring to a suspension of NaH (0.46 g, 19.2 mmol) in 3 mL of DMSO (Ar, 20 °C). The resulting suspension was stirred for 1 h at 20 °C, then a solution of tetrachloro-5,5-dimethoxycyclopentadiene (3.33 g, 12.6 mmol) in 3 mL of DMSO was added to it, and this mixture was stirred for an additional 5 h. The reaction mixture was quenched with 40 mL of H_2O, and the product was extracted with ethyl acetate (3×20 mL). The combined extracts were washed with a saturated solution of NaCl (20 mL), dried with $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on SiO_2 to give 2.88 g (60%) of **1**, R_f 0.5 (hexane—ethyl acetate, 9 : 1), m.p. 72—74 °C. IR, ν/cm^{-1}: 1620, 1660 (C=C). ^{1}H NMR ($CDCl_3$), δ: 0.83 (s, 3 H, CH_3); 0.96 (s, 3 H, CH_3); 1.03 (s, 3 H, CH_3); 1.05—1.00 (m, 2 H); 1.50—2.00 (m, 5 H); 3.23 (s, 3 H, OCH_3), 3.24 (s, 3 H, OCH_3); 4.75 (dd, 1 H, CHO, J = 3.3 Hz and 7.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 11.45 (CH_3); 20.19 (CH_3); 20.01 (CH_3); 33.22 (C-6'); 39.90 (C-3'); 44.92 (C-4'); 47.06 (C-7'); 49.60 (C-1'); 51.36 (OMe); 87.90 (C-2'); 96.76 (C-1); 105.40 (C-5); 128.05 (C-3); 129.60 (C-4); 146.60 (C-2). Found (%): C, 53.50; H, 6.08; Cl, 27.98. $C_{17}H_{23}Cl_3O_3$. Calculated (%): C, 53.47; H, 6.10; Cl, 27.92.

Decomposition of 1. Compound **1** (1 g, 2.62 mmol) was kept at ~20 °C for 30 days. During this period, the mixture gradually liquefied. The resulting oil was chromatographed on SiO_2; the product was eluted with a hexane—ethyl acetate mixture (9 : 1). This gave 0.52 g (80%) of (±)-2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-one (**2**) and 0.26 g (75%) of camphene (**3**).

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(±)-2,3,5-Trichloro-4,4-dimethoxycyclopent-2-en-1-one (2), m.p. 52—54 °C. IR (ν/cm^{-1}): 1600, 1750. ^{1}H NMR ($CDCl_3$), δ: 3.47 (s, 3 H, OCH_3); 3.49 (s, 3 H, OCH_3); 4.55 (s, 1 H, 5-H). ^{13}C NMR ($CDCl_3$), δ: 52.03 and 52.09 (OCH_3), 62.19 (C-5); 100.60 (C-4); 133.82 (C-2), 157.65 (C-3); 186.14 (C-1). MS (*m/z*): 244 $[M]^+$, 213 $[M-OCH_3]$, 209 $[M-Cl]$. Found (%): C, 34.13; H, 2.83; Cl, 43.45. $C_7H_7Cl_3O_3$. Calculated (%): C, 34.22; H, 2.85; Cl, 43.38.

(±)-2,2-Dimethyl-3-methylenebicyclo[2.2.1]heptane (3), m.p. 50—51 °C. ^{1}H NMR ($CDCl_3$) δ: 1.00 (s, 3 H, CH_3), 1.06 (s, 3 H, CH_3); 1.88 (m, 1 H, 4-H); 2.66 (m, 1 H, 1-H); 4.48 (s, 1 H, $C=CH_2$). ^{13}C NMR ($CDCl_3$), δ: 23.85 (C-6); 25.87 (CH_3); 28.95 (C-5); 29.45 (CH_3); 37.47 (C-7); 41.88 (C-2); 46.99 (C-4); 48.21 (C-1); 99.06 (C-3); 166.43 ($=CH_2$). The spectral characteristics of compound **3** coincided with those reported in the literature.[2,3]

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Competitive reactivity of vinylchalcogenyl radicals in their reactions with acetylene

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The reactivities of vinylthiyl and vinylselenyl radicals generated by high temperature gas-phase reactions of acetylene with diethyl disulfide and diethyl selenide, respectively, were compared. The co-pyrolysis of a mixture of these reagents at 410—510 °C results in a mixture of thiophene and selenophene. The vinylselenyl radical is more reactive; in addition, it appears to stabilize vinylthiyl radicals. Owing to this, co-thermolysis of diethyl disulfide, diethylselenide, and acetylene at 510 °C allows one to obtain simultaneously thiophene and selenophene in 91.0 and 92.5 % yields, respectively.

Key words: acetylene, gas-phase reactions, thiyl and selenyl radicals, thiophene, selenophene.

The thermolysis of the lowest dialkyl disulfides results in the generation of vinylthiyl radicals, which react with acetylene to give thiophene. The yield of the latter at 420—470 °C is 47—62 %.[1,2] Vinylselenyl radicals are efficiently generated in the thermolysis of dimethyl selenide. Their reactions with acetylene at 420—470 °C give selenophene in up to 90 % yields.[3] In a continuation of a study of the reactivity of thermally generated vinyl chalcogenyl radicals, we studied, under comparable conditions, the co-thermolysis of acetylene with diethyl disulfide (**1**), diethyl selenide (**2**), and their mixture (Table 1). The structure of the alkyl chain in these chalcogenides implies that the corresponding vinyl chalcogenyl radicals should be generated more efficiently from them than from other dialkyl chalcogenides.

The reaction of acetylene with diethyl disulfide at 480—500 °C results in thiophene in 45—50 % yield. This also gives side products, *i.e.*, thienothiophenes and aromatic hydrocarbons. Diethyl selenide reacts selectively with acetylene at 460 °C to give selenophene in an almost quantitative yield. The co-thermolysis of acetylene with a mixture of diethyl disulfide and diethyl selenide occurs in a somewhat different way. The main reaction products include sulfur disulfide, thiophene, and selenophene. Their yields and ratio depend considerably on the reaction temperature. At 410 °C and with incomplete conversion of diethyl disulfide, carbon disulfide is the main reaction product (Table 1).[1] Thiophene and selenophene are formed in nearly equal yields. The difference in the reactivities of the vinylthiyl and

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