A novel variant for the preparation of allyl(propargyl) vinyl ethers and their rearrangement into 5-allyl(allenyl)-5-chloro-2-(2-hydroxyethyloxy)-cyclopent-2-ene-1,4-diones

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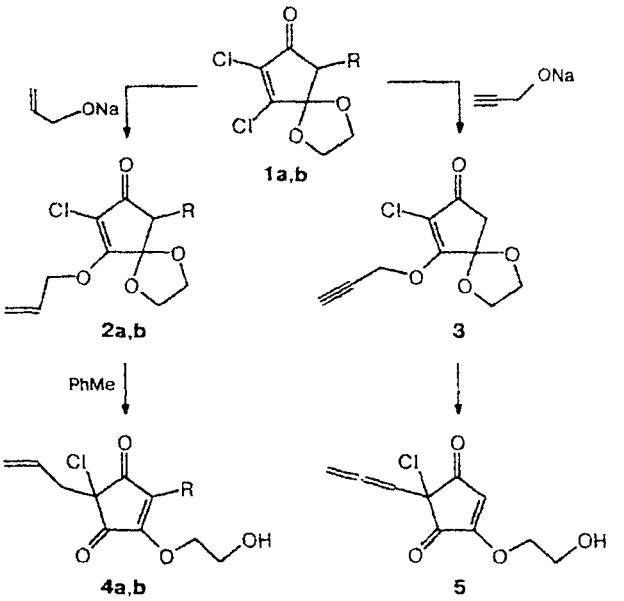
Reactions of 1,2-di- and 1,2,4-trichloro-6,9-dioxaspiro[4.4]non-1-en-3-ones with sodium 2-propenoxide or sodium 2-propynoxide afforded the corresponding 3-allyloxy or 3-propynyloxycyclopentenones, as well as the products of their subsequent thermal [3,3]-sigmatropic rearrangement.

Key words: trichlorocyclopentenones, 2-propenoxide and propynoxide anions, allyl vinyl ethers, Claisen rearrangement, cyclopentendiones.

[3,3]-Sigmatropic rearrangement of allyl vinyl ethers (Claisen rearrangement)[1] is an acknowledged and widely used in organic synthesis method for the formation of the C—C-bond.[2,3] Known variations of this reaction involve Claisen anoinoid hydroxy-rearrangement,[4] Ireland *o*-silylacetal method,[5] Eschenmoser amidoacetal method,[6] aza-,[7] thia-rearrangement,[8] *etc.*[9] There are no significant restrictions for the structures of substrates involved in the rearrangement. The main difficulty is generation of necessary substrates of the allyl vinyl type. $Hg(OAc)_2$-catalyzed *trans*-etherification of ethyl vinyl ether with allylic alcohols,[10] synthesis of ketone Si-, N-, and O-acetals from allyl-containing esters and amides,[2,3,11] acid-catalyzed reactions of ethyl orthoacetate[12] and enamines[13] with allyl alcohols, *etc.* are among the methods for the generation of such substrates.

Taking into account the tendency of chlorides **1a,b**[14,15] to enter into substitution reactions of the vinyl Cl atom at the C(3) atom with various N-, O-, and S-nucleophiles,[16] in this work we have synthesized the corresponding vinyl ethers of allyl and propargyl alcohols and studied them under thermal Claisen rearrangment conditions. Vinylation of the alcohols **1a,b** according to the procedure developed recently[16] afforded ethers **2a,b** and **3** in 61, 32, and 84% yield, respectively.

The mechanism of the developed tandem process is obvious. 2,3-Dichlorocyclopentenones **1a,b** react with anions of allyl and propargyl alcohols according to the scheme of conjugated 1,4-addition, the intermediate Michael enolates formed being stabilized by the elimination of Cl^- at the C(3) atom (the Ad_NE-mechanism). The effective one-step approach to vinyl ethers **2a,b** and **3** is thereby realized. Thermal Claisen rearrangement of ethers **2a,b** and **3** proceeds upon boiling of their toluene solutions and involves simultaneous opening of the dioxolan cycle and dehydrogenation to give cyclopentenediones **4a,b** and **5**. The latter are of interest as a key compound in the synthesis of a series of natural cyclopentanoids.



R = H (**a**), Cl (**b**)

Experimental

IR spectra were obtained on an UR-20 spectrophotometer in thin layer or as suspension in nujol. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300

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(^{1}H) and 75.47 MHz (^{13}C)) in $CDCl_3$ with $SiMe_4$ as the internal standard.

Synthesis of vinyl ethers 2a,b and 3 (general procedure). A solution of dichloroketone **1a** or **1b** (9.5 mmol) in THF (5 mL) was added to a solution of sodium alcoxide prepared from NaH (0.19 g, 7.9 mmol) and allyl or propargyl alcohol (3 mL), in dry THF (2 mL) with stirring. The reaction mixture was kept at ~20 °C for 30 min, water was added, and the mixture was extracted with CH_2Cl_2. The combined extracts were washed with H_2O, dried with $MgSO_4$, concentrated, and the residue was chromatographed on SiO_2 (pentane—ethyl acetate, 1 : 1).

(±)-1-Allyloxy-2-chloro-6,9-dioxaspiro[4.4]non-1-en-3-one (2a). The yield was 61%. Found (%): C, 52.22; H, 4.57; Cl, 15.56. $C_{10}H_{11}ClO_4$. Calculated (%): C, 52.07; H, 4.81; Cl, 15.37. IR (ν/cm^{-1}): 1480, 1640, 1670, 1760. ^{1}H NMR ($CDCl_3$), δ: 2.72 (s, 2 H, CH_2); 4.0—4.2 (m, 4 H, 2 CH_2O); 5.08—5.14 (m, 2 H, CH_2O); 5.26—5.43 (m, 2 H, CH_2=); 5.88—6.04 (m, 1 H, CH=). ^{13}C NMR, δ: 44.71 (C-5); 66.39 (C-7, C-8); 72.25 (CH_2O); 107.72 (C-3); 109.37 (C-1); 119.10 (CH_2=); 131.43 (CH=); 172.82 (C-2); 192.98 (C-4).

(±)-1-Allyloxy-2,4-dichloro-6,9-dioxaspiro[4.4]non-1-en-3-one (2b). The yield was 32%. Found (%): C, 45.33; H, 3.71; Cl, 26.60. $C_{10}H_{10}Cl_2O_4$. Calculated (%): C, 45.28; H, 3.77; Cl, 26.79. IR (ν/cm^{-1}): 1475, 1640, 1755, 3030. ^{1}H NMR ($CDCl_3$), δ: 4.12—4.30 (m, 4 H, 2 CH_2O); 4.51 (s, 1 H, H-5); 5.15—5.20 (m, 2 H, CH_2O); 5.35—5.48 (m, 2 H, CH_2=); 5.93—6.07 (m, 1 H, CH=). ^{13}C NMR ($CDCl_3$), δ: 61.10 (C-5); 67.02 (C-7); 67.15 (C-8); 72.94 (CH_2O); 106.92 (C-3); 109.51 (C-1); 119.73 (CH_2=); 131.17 (CH=C); 170.28 (C-2); 187.26 (C=O).

(±)-2-Chloro-1-(2-propynyloxy)-6,9-dioxaspiro[4.4]non-1-en-3-one (3). The yield was 84%. Found (%): C, 52.45; H, 4.00; Cl, 15.75. $C_{10}H_9ClO_4$. Calculated (%): C, 52.51; H, 3.93; Cl, 15.53. IR (ν/cm^{-1}): 1480, 1640, 1730, 2150, 3270. ^{1}H NMR ($CDCl_3$), δ: 2.67 (s, 1 H, HC≡); 2.69 (s, 2 H, CH_2); 4.00—4.20 (m, 4 H, OCH_2CH_2O); 5.17 (d, 1 H, HC≡, J = 2.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 59.03 (CH_2); 66.22 (C-7); 76.12 (C≡); 78.31 (HC≡); 107.21 (C-1); 110.01 (C-1); 171.23 (C-2); 192.34 (C-4).

Claisen rearrangement (general procedure). A solution of vinyl ether (**2a,b** or **3**) (0.5 g) in toluene (10 mL) was refluxed for 6 h. The solvent was removed and the residue was purified by chromatography on SiO_2 (pentane—AcOEt, 1 : 1).

(±)-5-Allyl-5-chloro-2-(2-hydroxyethyloxy)cyclopent-2-en-1,4-dione (4a). The yield was 75%. Found (%): C, 51.92; H, 4.67; Cl, 15.16. $C_{10}H_{11}ClO_4$. Calculated (%): C, 52.07; H, 4.81; Cl, 15.37. IR (ν/cm^{-1}): 1600, 1640, 1708, 1748, 3088, 3600. ^{1}H NMR ($CDCl_3$), δ: 2.70—2.86 (m, CH_2); 3.76—4.05 (m, 1 H, OH); 3.95—4.05 (m, 2 H, CH_2O); 4.20—4.30 (m, 2 H, CH_2O); 5.07—5.18 (m, 2 H, CH_2=); 5.44—5.60 (m, 1 H, CH=); 6.39 (s, 1 H, H-5). ^{13}C NMR ($CDCl_3$), δ: 38.74 (CH_2); 60.06 (CH_2O); 61.53 (CH_2O); 74.13 (C-3); 118.06 (C-3); 122.10 (CH=); 128.74 (CH_2=); 169.65 (C-2); 192.15 (C-1); 192.93 (C-4).

(±)-5-Allyl-3,5-dichloro-2-(2-hydroxyethyloxy)cyclopent-2-en-1,4-dione (4b). The yield was 69%. Found (%): C, 45.35; H, 3.80; Cl, 26.65. $C_{10}H_{10}Cl_2O_4$. Calculated (%): C, 45.28; H, 3.77; Cl, 26.79. IR (ν/cm^{-1}): 1600, 1640, 1748, 3088, 3600. ^{1}H NMR ($CDCl_3$), δ: 2.71—2.84 (m, 2 H, CH_2); 3.02—3.18 (m, 1 H, OH); 3.85—3.93 (m, 2 H, CH_2O); 4.08—4.25 (m, 2 H, CH_2O); 5.07—5.18 (m, 2 H, CH_2=); 5.38—5.57 (m, 1 H, CH=); 6.04 (s, 1 H, C(5)H). ^{13}C NMR ($CDCl_3$), δ: 38.99 (CH_2); 61.16 (C-6); 62.43 (C-8); 74.55 (C-5); 122.30 (CH=); 128.49 (CH_2=); 131.00 (C-3); 162.74 (C-2); 186.54 (C-1); 188.99 (C-4).

(±)-5-Chloro-2-(2-hydroxyethyloxy)-5-propadienylcyclopent-2-en-1,4-dione (5). The yield was 52%. Found (%): C, 52.30; H, 3.89; Cl, 15.63. $C_{10}H_9ClO_4$. Calculated (%): C, 52.51; H, 3.93; Cl, 15.53. IR (ν/cm^{-1}): 1350, 1610, 1720, 1775, 2950, 3600. ^{1}H NMR ($CDCl_3$), δ: 3.11 (m, 1 H, OH); 3.96 (t, 2 H, CH_2OH, J = 4.07 Hz); 4.20 (t, 2 H, CH_2O, J = 4.17 Hz); 4.98 (d, 2 H, =CH_2, J = 6.59 Hz); 5.36 (t, 1 H, =CH, J = 6.59 Hz); 6.29 (s, 1 H, H-3). ^{13}C NMR ($CDCl_3$), δ: 60.15 (CH_2); 74.24 (C-5); 80.79 (=CH_2); 87.01 (=CH); 116.68 (C-2); 168.63 (C-3); 189.63 (C-4); 190.79 (C-1); 208.68 (=C=).

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