Thietane and Selenetane Complexes by Thermal Cycloaddition of Vinyl Ethers to Transition Metal Coordinated Thio- and Seleno-aldehydes

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Pentacarbonyl tungsten coordinated thio- and seleno-benzaldehydes react with vinyl ethers by regiospecific addition of the C=C to the X=C bond of the heteroaldehydes to form thietane and selenetane complexes, respectively.

Thio- and seleno-aldehydes not stabilized by either very bulky substituents or by mesomeric effect of heteroatoms such as nitrogen or sulfur are unstable and immediately oligomerize.[1,2] This considerably restricts their potential use in organic synthesis. Therefore, until now only inter-[3,4] or intra-molecular [4 + 2] cycloadditions[3,5,6] with conjugated dienes (trapping of the intermediates) and ene reactions[3,6,7] are known. In addition, the reactions of the isolable 2,4,6-tri-*tert*-butylthiobenzaldehyde with Grignard and organolithium reagents have also been studied.[8]

The problems connected with the high reactivity of the heteroaldehydes can be circumvented by using their complexes. Heteroaldehydes stabilized by coordination to a $(CO)_5W$ or $(CO)_5Cr$ fragment are conveniently accessible building blocks. They readily react with (*i*) electron-rich alkynes by regiospecific [2 + 2] cycloaddition and subsequent stereospecific electrocyclic ring-opening to give heteroacrylic acid derivatives[9] and (*ii*) with conjugated dienes by [4 + 2] cycloaddition to form six-membered heterocycles.[10] The coordination to the $(CO)_5M$ fragment strongly influences the stereoselectivity of the Diels–Alder reaction.[11] We now report the first thermal [2 + 2] cycloaddition of vinyl ethers to metal-coordinated thio- and seleno-aldehydes. The reactions proceed regiospecifically and stereoselectively to give thietane and selenetane complexes, respectively.

The heteroaldehyde complexes **1a** and **b** react with ethyl vinyl ether **2** even at −20 °C within several hours to form 1 : 1 adducts. The progress of the reaction can be followed easily by IR spectroscopy or by monitoring the colour change of the solution from deep-red to orange. After column chromatography on silica gel the thietane and selenetane complexes **4a** and **b**,[†] respectively, are obtained as yellow oils in more than 80% yield. The addition of **2** to the X=C bond of **1** is regiospecific. In the resulting heterocycles the H(EtO)C-group of **2** is bonded to the heteroatom X. According to the ^1H NMR spectra, which are in the range from −95 to 20 °C independent of the temperature, both substituents (OEt and Ph) are mutually *cis* thus minimizing steric interaction with the bulky pentacarbonylmetal fragment on X.

The initial reaction products, however, are the isomeric complexes **3a**, **a′** and **3b**, **b′**,[†] respectively, as can be shown by the NMR spectra of the crude reaction mixture. At room temperature **3a** and **a′** rapidly interconvert [$\Delta G^\ddagger$ = 44 kJ mol^{-1} (at −30 °C)]. The interconversion for **3b**, **b′** is slow on the NMR time scale even at room temperature [$\Delta G^\ddagger > 58$ kJ mol^{-1}]. In both isomers, **3** and **3′**, the substituents OEt and Ph occupy mutual *trans* positions. The reaction rate for the addition of **2** to **1a**, which initially gives the sterically more demanding '*trans*' complexes, is only slightly solvent depen-

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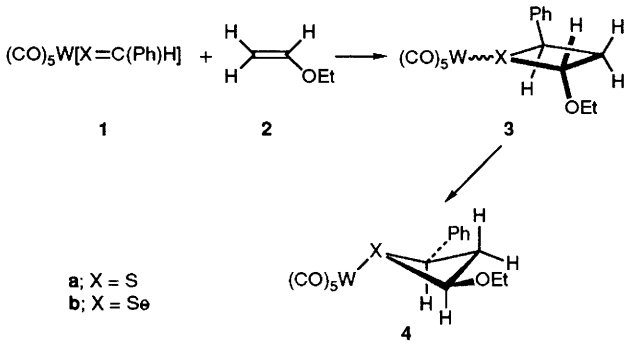
[†] *Selected ^1H NMR data*: **4a** δ ($CDCl_3$) 3.17 (ddd, *J* 13.1, 10.1 and 7.7 Hz, 1 H, CH_2), 3.43 (ddd, *J* 13.1, 8.1 and 6.9 Hz, 1 H, CH_2), 4.47 [dd, *J* 10.1 and 8.1 Hz, C(Ph)*H*] and 5.37 [dd, *J* 7.6 and 6.9 Hz, C(OEt)*H*]; **4b**: δ ($CDCl_3$, −10 °C) 3.54 (ddd, *J* 13.9, 11.1 and 8.5 Hz, 1 H, CH_2), 3.95 (ddd, *J* 13.9, 7.9 and 6.6 Hz, 1 H, CH_2), 4.65 [dd, *J* 11.1 and 7.8 Hz, C(Ph)*H*] and 5.57 [dd, *J* 8.4 and 6.5 Hz, C(OEt)*H*]; **3a/a′** ($CDCl_3$, −90 °C): **3a**: δ 4.75 [dd, *J* 9.9 and 3.6 Hz, C(Ph)*H*] and 6.06 [dd, *J* 7.1 and 6.9 Hz, C(OEt) *H*]; **3a′**: δ 5.40 [dd, *J* 8.5 and 8.4 Hz, C(Ph)*H*] and 5.50 [dd, *J* 6.7 and 2.7 Hz, C(OEt) *H*]; **3b/b′** ($CDCl_3$, −30 °C): **3b**: δ 4.60 [dd, *J* 10.0 and 3.6 Hz, C(Ph)*H*] and 5.93 [dd, *J* 7.6 and 7.0 Hz, C(OEt)*H*]; **3b′**: δ 5.19 [dd, *J* 6.7 and 2.7 Hz, C(OEt)*H*] and 5.63 [dd, *J* 9.4 and 9.1 Hz, C(Ph)*H*].



dent [k(pentane) : k(toluene) : $k(CH_2Cl_2)$ = 1 : 1.8 : 2.4]. When *cis*-[$^2H_1$] **2** is employed instead of **2**, the *cis* arrangement of D and OEt is preserved in [$^2H_1$] **3a**, **a'** (Ph and D being *trans*). Conversely, the reaction of **1a** with *trans*-[$^2H_1$] **2** gives [$^2H_1$] **3a**, **a'** with OEt and D *trans* and Ph and D *cis*. Therefore, diradical or dipolar intermediates involving rotation around the (EtO)C–CH_2 bond can be excluded. The results can be explained by a nonsynchronous concerted [$2\pi_s + 2\pi_a$] process or by a [2 + 2 + 2] process (additionally involving the lone electron pair at the heteroatom X).

At room temperature in $CDCl_3$ the complexes **3** isomerize completely within several hours to form **4**. The rearrangement is acid-catalysed and very likely proceeds by protonation of OEt, subsequent elimination of EtOH, and readdition of EtO^-–EtOH. In agreement with such a sequence an exchange (*i*) of OC_2H_5 for OC_2D_5 in C_2D_5OD–CF_3CO_2D and (*ii*) of OC_2H_5 for OCH_3 in CH_3OH/CF_3CO_2H is observed.

Apart from **2** other vinyl ethers, *e.g.* butyl vinyl ether and 1- and 2-substituted vinyl ethers [*e.g.* 2-methoxypropene, α-methoxystyrene, *cis*- and *trans*-H(Me)C=C(OEt)H] also add to the X=C bond of **1** to form the corresponding thietane and selenetane complexes in high yield.

The reactivity of thietane complexes has recently attracted considerable interest.[12] Until now, thietane and selenetane complexes were prepared by ligand substitution reactions. However, only a few methods for the preparation of selenetanes are available. Apart from selenetane itself, only 3-mono- and 3,3-di-substituted selenetanes are known. Therefore, the reaction of metal-coordinated thio- and selenoaldehydes with electron-rich alkenes considerably extends the accessible substitution pattern of thietane and selenetane ligands and offers a convenient route for the synthesis of their complexes.

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