Selenoaldehydes Formed by 1,2-Elimination and Trapped as Diels–Alder Adducts

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Various selenenyl derivatives, $RO_2C{\cdot}CH_2SeX$, underwent elimination with triethylamine to form selenoaldehydes, $RO_2C{\cdot}CHSe$, which were trapped *in situ* as cycloadducts with conjugated dienes; the adduct of ethyl selenoxoacetate and anthracene dissociated upon heating thereby allowing transfer of the selenoaldehyde to 2,3-dimethylbuta-1,3-diene.

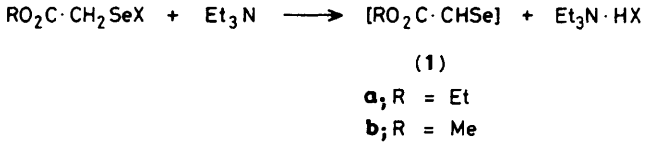
Reactive thioaldehydes, ZCHS, may be formed and trapped *in situ* as cycloadducts with conjugated dienes, by base-mediated 1,2-elimination of HX from sulphenyl derivatives, ZCH_2SX, where Z is generally an electron-withdrawing group.[1] We now report that transient selenoaldehydes (**1**) may likewise be formed from selenenyl derivatives (Scheme 1). Also, the cycloadduct (**11a**) of ethyl selenoxoacetate (**1a**) and anthracene dissociates at 80 °C, thus serving as a convenient, 'clean' precursor of the selenoaldehyde.

Appropriate precursors (**3**), (**5**), (**6**), and (**7**) for the

Table 1. Cycloadducts of conjugated dienes and the selenoaldehyde (**1a**) formed from the phthalimido precursor (**6a**).

Diene	Cycloadduct[d]	Yield/%	B.p. (Kugelrohr distillation pressure) or m.p. (solvent for crystallisation)
Cyclopentadiene	(**9a**)	64[a]	130—135 °C (0.3 mm Hg)
2,3-Dimethylbuta-1,3-diene	(**8a**)[b]	54	120 °C (0.035 mm Hg)
Cyclohexa-1,3-diene	(**10a**)	26[c]	158—160 °C (0.1 mm Hg)
Anthracene	(**11a**)	32	147—149 °C (Et_2O)

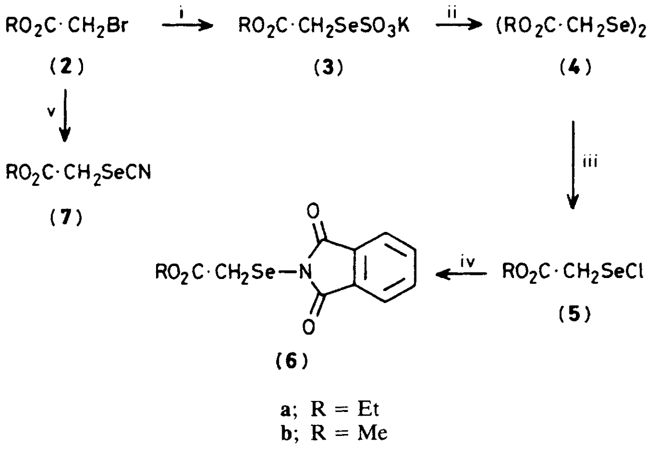
[a] Mixture of *endo* and *exo* isomers (*ca.* 1:1). [b] Similarly: (**8b**), 45%, b.p. 150—155 °C (0.8 mm Hg). [c] Mixture of *endo* and *exo* isomers (*ca.* 8:2). [d] Selected ^1H n.m.r. data ($CDCl_3$) ($^2J_{HSe}$ obtained from ^{77}Se satellites): *endo*-(**9a**), δ 4.71 (d, *J* 3.9, J_{HSe} 15.4 Hz, 3-H); *exo*-(**9a**). δ 3.57 (s. J_{HSe} 12.1 Hz, 3-H); (**8a**), δ 3.68 (dd. 8.5, 4.9, J_{HSe} 13.3 Hz, 2-H); (**8b**), δ 3.81 (dd, *J* 7.5, 5.5 Hz, 2-H); *endo*-(**10a**), δ 4.35 (d, *J* 2.9 Hz, 3-H); (**11a**), δ 5.32 (s, 10-H), 4.93 (d, *J* 3.0 Hz, 9-H), and 4.35 (d, *J* 3.0 Hz, 12-H).



Scheme 1

selenoaldehydes (**1**) were prepared† as shown in Scheme 2. Thus, ethyl bromoacetate (**2a**) and potassium selenosulphate[2] in hot aqueous ethanol gave[3] the 'seleno Bunte salt' (**3a**) (66%), m.p. 143—147 °C (decomp.), which was oxidized with iodine to give the diselenide (**4a**) (79%), b.p. 86—90 °C (0.2 mm Hg), δ ($CDCl_3$) 3.73 (s, $SeCH_2$). Cleavage[4] with sulphuryl chloride in benzene gave the red-brown selenenyl chloride (**5a**), δ ($CDCl_3$) 4.22 (s, $SeCH_2$), as an unstable oil, which was redissolved in an appropriate solvent for immediate use. Thus, treatment[5] with an excess of freshly prepared potassium phthalimide in 1,2-dichloroethane with cooling in ice gave the phthalimido derivative (**6a**) [41% yield from (**4a**)], m.p. 111—114 °C, δ ($CDCl_3$) 3.72 (s, $SeCH_2$). Finally, heating ethyl bromoacetate and potassium selenocyanate in ethanol gave the selenocyanate (**7**) (65%), b.p. 72—78 °C (0.25 mm Hg), δ ($CDCl_3$) 3.83 (s, $SeCH_2$). The methyl esters (**3b**), (**4b**), (**5b**), and (**6b**) were prepared similarly.

Preliminary experiments on the formation and trapping of the selenoaldehyde (**1a**), under conditions that afforded high yields for thioaldehydes,[1] gave disappointing results. For example, slow addition of the selenenyl chloride (**5a**) in benzene to 2,3-dimethylbuta-1,3-diene in benzene–methanol containing triethylamine *at room temperature*[1a] gave a complex mixture containing only small quantities (5—10%) of the cycloadduct (**8a**). However, when the selenenyl chloride was added slowly to the same mixture *with heating under reflux* the product consisted largely of the diselenide (**4a**) and the cycloadduct (**8a**), in approximately equal amounts; the latter was isolated in 36% yield. Again, addition of triethylamine to the 'seleno Bunte salt' (**3a**), dimethylbutadiene, and calcium chloride dihydrate in refluxing ethanol gave the same cycloadduct (**8a**) (30%), whereas the yield was minimal at room temperature.[1c] The selenocyanate (**7a**) also gave the cycloadduct (**8a**) under the conditions employed for the 'seleno Bunte salt.'



Scheme 2. *Reagents*: i, K_2SeSO_3, H_2O–ROH; ii, I_2, H_2O–EtOH; iii, SO_2Cl_2, C_6H_6, 20 °C; iv, potassium phthalimide, $ClCH_2CH_2Cl$, 20 °C; v, KSeCN, EtOH.

The crystalline phthalimido derivative (**6a**) was selected for studies with a range of dienes, since the corresponding sulphur compound[1b] had yielded ethyl thioxoacetate cleanly at room temperature with catalytic amounts of triethylamine. However, a higher reaction temperature again proved beneficial. Triethylamine (0.064 mmol) in benzene (3 ml) was added slowly to the precursor (**6a**) (0.64 mmol) and the diene (3.2 mmol) in benzene (10 ml) with heating under reflux. The yields of isolated cycloadducts are in Table 1. Cycloaddition of maleic anhydride to cyclopentadiene, 2,3-dimethylbuta-1,3-diene, cyclohexa-1,3-diene, and anthracene occurs at rates decreasing in this order.[6] The yields of the corresponding selenoaldehyde adducts are therefore consistent with the trapping of a labile, dienophilic intermediate. In particular, isolation of the adducts (**9a**) in 64% yield implies efficient generation of ethyl selenoxoacetate (**1a**), although conditions for its effective trapping are clearly more demanding than those for the corresponding thioaldehyde.‡ The structures of the cycloadducts were determined from their spectra, which resembled those of the thioaldehyde adducts.[1] Additionally, the oily esters (**8a**) and (**8b**) were hydrolysed to give the same crystalline acid (**8**; R = H), m.p. 85—87 °C.

The anthracene adduct (**11a**) was most conveniently prepared [28% overall yield from (**4a**)] by slow addition of the

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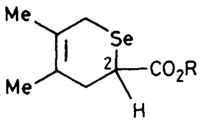
† All new compounds were characterised spectroscopically and, apart from the selenenyl chlorides, which were used without purification, by combustion analysis for C, H, and, where appropriate, N.

‡ Minor products accompanying the adducts (**8a**), (**9a**), and (**10a**) have been identified as the corresponding cycloadducts of the diselenoester, $EtO_2C·CH_2SeC(=Se)CO_2Et$.



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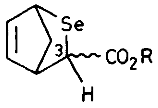

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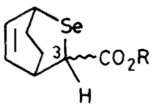

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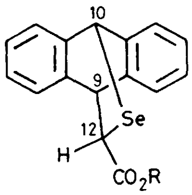

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selenenyl chloride (**5a**) to anthracene (5 mol equiv.) in chloroform with heating under reflux. This adduct (**11a**), though stable to crystallisation from hot solvents and during storage at room temperature, dissociated reversibly in benzene at 80 °C. When heated for 64 h with dimethylbutadiene (1.2 mol equiv.) in benzene under reflux the adduct (**11a**) gave the selenin (**8a**) in high yield (64% isolated), and anthracene. The generation of selenoaldehydes by retro-Diels–Alder reactions provides therefore an alternative, 'clean' method for further studies on their chemistry.

Selenoladehydes stabilised by electron-donating groups were reported[7] in 1979 but, until very recently,[8] the chemistry of simple, labile selenoaldehydes was largely unexplored. Fischer *et al.*[9] prepared chromium and tungsten complexes of selenobenzaldehydes, ArCH=SeM(CO)$_5$, and showed that they reacted with cyclopentadiene and 2,3-dimethylbuta-1,3-diene to give the corresponding cycloadduct complexes. Krafft and Meinke[8] have described the first preparative route to simple selenoaldehydes. They cleaved α-(phenyldimethylsilyl) selenocyanates with tetrabutylammonium fluoride in the presence of cyclopentadiene to obtain cycloadducts of the selenoaldehydes, generally in good yield.

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