Reactive Selenoaldehydes Formed from Selenenyl Derivatives by 1,2-Elimination and Trapped *in situ* as Cycloadducts with Conjugated Dienes

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Selenenyl derivatives, ZCH_2SeX, where Z is an electron-withdrawing group (Z = EtO_2C, MeO_2C, PhCO, PhNHCO, or NC) and X is a leaving group (X = CN, SO_3K, Cl, SO_2Tol, and *N*-phthalimido), react with triethylamine to form selenoaldehydes, ZCHSe, by 1,2-elimination of HX. The transient selenoaldehydes can be trapped *in situ* as cycloadducts with the conjugated dienes 2,3-dimethylbuta-1,3-diene, cyclopentadiene, cyclohexa-1,3-diene, the alkaloid thebaine (**27**), anthracene, and 9,10-dimethylanthracene. Efficient trapping (>60%) has been achieved only with cyclopentadiene and dimethylanthracene. Certain of the cycloadducts, *e.g.* those from dimethylbutadiene, are accompanied by lesser amounts of the cycloadducts of diselenoesters, *e.g.* $EtO_2CCH_2SeC(=Se)CO_2Et$. The cycloadducts of cyclopentadiene, anthracene, and 9,10-dimethylanthracene dissociate at 80—120 °C to release the selenoaldehydes, which can be trapped *in situ* in high yield with dimethylbutadiene. The ease of formation and trapping, and the stereoselectivity in cycloadditions, of selenoaldehydes are compared with the corresponding properties of analogous thioaldehydes.

Selenoaldehydes, like thioaldehydes, are generally too reactive to be isolated or manipulated at ambient temperatures. Indeed, the only stable derivatives known[1] at present have the selenoformyl group attached to strongly electron-donating, heterocyclic rings and are, in effect, vinylogous selenoamides. However, reactive thioaldehydes, ZCHS, may be readily formed,[2] 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. This group facilitates elimination, ensures rapid reaction of the transient thioaldehyde with the common, electron-rich dienes, and provides a convenient functional group for subsequent transformations of the cycloadducts. It seemed that a similar strategy might extend the currently meagre chemistry of simple selenoaldehydes. We report here our first studies on the formation of transient selenoaldehydes from selenenyl derivatives (Scheme 1).† The selenoaldehydes, ZCHSe

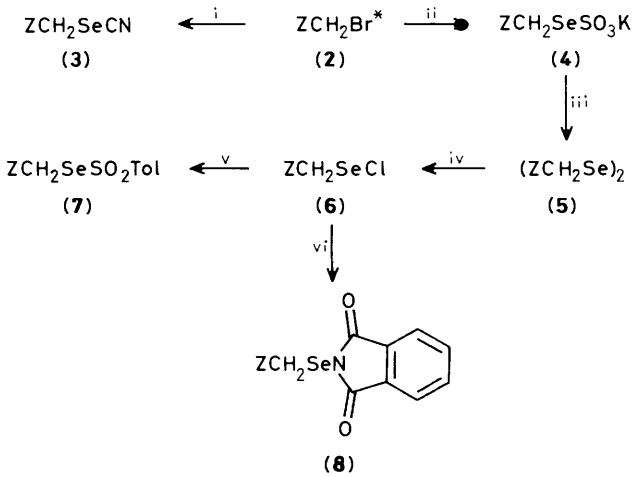
$$ZCH_2SeX + Et_3N \longrightarrow [ZCHSe] + Et_3N{\cdot}HX$$
(1)

a; Z = EtO_2C
b; Z = MeO_2C
c; Z = PhCO
d; Z = PhNHCO
e; Z = NC

Scheme 1.†

(**1**) (Z = EtO_2C, MeO_2C, PhCO, PhNHCO, or NC) were trapped *in situ*, like the corresponding thioaldehydes, with various conjugated dienes. Again, the bridged cycloadducts of cyclopentadiene, anthracene, and 9,10-dimethylanthracene were found to release the selenoaldehydes at convenient temperatures, 80—120 °C, and thus serve as 'clean,' ancillary precursors of these labile species.

Preparation of Selenoaldehyde Precursors (*Schemes* 1 *and* 2).—Suitable precursors, (**3**), (**4**), (**6**), (**7**), and (**8**) for the selenoaldehydes were prepared as shown in Scheme 2. All but one class, the selenocyanates (**3**), were analogous to those sulphenyl derivatives shown to act as precursors for thioaldehydes.[3] A complete set of precursors for ethyl selenoxoacetate (**1a**) was prepared as follows. Ethyl bromoacetate (**2a**) reacted with potassium selenosulphate,[4] obtained from selenium and potassium sulphite, in hot aqueous ethanol to give[5] the 'seleno Bunte salt' (**4a**) (66%), which was oxidised with iodine to afford the diselenide (**5a**) (79%) cleanly. An alternative route to (**5a**), from the bromo ester (**2a**) and disodium diselenide, was unsatisfactory, giving mixtures of the diselenide (**5a**) and the corresponding monoselenide. Cleavage[6] of the diselenide (**5a**) with sulphuryl chloride in benzene gave the selenenyl chloride



a; Z = EtO_2C, Tol = 4-MeC_6H_4 throughout
b; Z = MeO_2C
c; Z = PhCO
d; Z = PhNHCO
e*; Z = NC

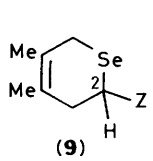
Scheme 2. *Reagents:* i, KSeCN, EtOH; ii, K_2SeSO_3, H_2O–EtOH, or H_2O–MeOH; iii, I_2, H_2O–EtOH; iv, SO_2Cl_2, C_6H_6, 20 °C; v, $TolSO_2Na$, EtOH–C_6H_6; vi, K phthalimide, $ClCH_2CH_2Cl$, 20 °C. * Exceptionally, (**2e**) = $NCCH_2Cl$

† We cannot exclude the possibility that triethylamine acts first by displacing the leaving group, X, from selenium and then by eliminating triethylamine and a proton from the resulting quaternary ammonium intermediate.

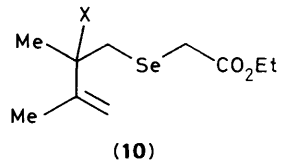
(**6a**) as a red-brown, unstable oil, which was redissolved in an appropriate solvent for immediate use. Thus, this selenenyl chloride (**6a**), with sodium toluene-*p*-sulphinate in ethanol–benzene, or with potassium phthalimide in 1,2-dichloroethane,[7] gave the oily selenotoluene-*p*-sulphonate (**7a**) or the crystalline phthalimido derivative (**8a**), respectively. Attempted purification of the selenosulphonate (**7a**) led to partial decomposition, consequently this precursor, like the chloride (**6a**), was prepared immediately before use. Finally, ethyl bromoacetate and potassium selenocyanate in hot ethanol gave the oily selenocyanate (**3a**). The methyl esters (**4b**), (**5b**), (**6b**), and (**8b**) were prepared similarly. A limited selection of precursors for the other selenoaldehydes (**1c—e**) was obtained as follows: phenacyl bromide (**2c**) gave the selenocyanate (**3c**),[8] *N*-(bromoacetyl)aniline (**2d**) the selenosulphate (**4d**), and chloroacetonitrile (**2e**) the selenosulphate (**4e**).

Formation and Trapping of Ethyl Selenoxoacetate.—The formation and trapping of ethyl selenoxoacetate (**1a**) was studied first, to establish appropriate conditions for the generation of other selenoaldehydes and to provide comparisons with the well developed chemistry[2] of the corresponding thioaldehyde. Preliminary experiments on the formation of the selenoaldehyde (**1a**), using conditions that afforded high yields of the thioaldehyde, gave disappointing results. For example, the selenenyl chloride (**6a**) was added in benzene to 2,3-dimethylbuta-1,3-diene (5 mol equiv.) in benzene–ethanol containing triethylamine at *room temperature*. The colour of the selenenyl chloride was rapidly discharged, but a complex mixture of products was obtained containing only small amounts (5—10%) of the cycloadduct (**9a**). However, when the selenenyl chloride was added slowly to the same mixture *with heating under reflux* the product consisted largely of the diselenide (**5a**) and the cycloadduct (**9a**), in approximately equal amounts; the cycloadduct was isolated in 36% yield. Again, addition of triethylamine to the selenosulphate (**4a**), dimethylbutadiene (5 mol equiv.), and calcium chloride dihydrate (added to remove the nucleophilic sulphite dianion as its insoluble calcium salt[3b]) in refluxing ethanol gave the same cycloadduct (**9a**) (30%), whereas the yield was minimal at room temperature.

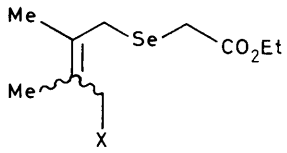
Formation of the cycloadduct (**9a**) in the foregoing experiments is evidence for the transient existence of the selenoaldehyde (**1a**). However, this adduct might, in principle, have arisen indirectly from electrophilic attack by the selenenyl derivatives, EtO_2CCH_2SeX, on the diene to give intermediates which were subsequently cyclised by triethylamine. This point was tested with the two most reactive precursors,* the selenotoluene-*p*-sulphonate (**7a**) and the selenenyl chloride (**6a**). The selenosulphonate (**7a**) was added slowly to dimethylbutadiene (5 mol equiv.) in ethanol containing triethylamine (1 mol equiv.) and calcium chloride (1 mol equiv.) with heating under reflux. The cycloadduct (**9a**) was obtained in 59% yield. In contrast, when triethylamine was added slowly to the selenosulphonate (**7a**), dimethylbutadiene, and calcium chloride, under the same conditions, the major product was the ethoxy selenide (**10**; X = EtO), accompanied by only small amounts of the cycloadduct. Clearly, when the concentration of triethylamine is low, electrophilic attack by the selenosulphonate (**7a**) on the diene can compete with elimination (Scheme 1) to form the selenoaldehyde, but the resulting 1,2-adduct (**10**; X = EtO) does not undergo cycloelimination to any great extent. In a second set of control experiments, the selenosulphonate was added slowly to dimethylbutadiene (5 mol equiv.) and triethylamine in refluxing benzene, rather than ethanol. The cycloadduct (**9a**) was obtained in 22% yield. In contrast, when



(**9**)



(**10**)



(**11**)

the selenosulphonate and the diene were heated in benzene in the absence of triethylamine, a complex mixture of products, containing the stereoisomeric 1,4-adducts (**11**; X = $TolSO_2$) (*ca.* 1:1) but no cycloadduct (**9a**), was obtained. This mixture was unchanged when heated with triethylamine in benzene. Further, a purified sample of the mixture of stereoisomers (**11**; X = $TolSO_2$) was unaffected by heating in ethanol with triethylamine. Similar results were obtained with the selenenyl chloride (**6a**). This reacted with dimethylbutadiene in benzene to give complex mixtures both at room temperature and at 80 °C. A small quantity of the 1,2-adduct (**10**; X = Cl) was isolated from the mixture formed at room temperature. The ^1H n.m.r. spectrum of the mixture formed at 80 °C suggested the presence of the 1,4-adducts (**11**; X = Cl). When this latter mixture was heated in benzene with triethylamine, no significant amounts of the cycloadduct (**9a**) were formed, although this cycloadduct was obtained by addition of the selenenyl chloride to a preformed mixture of the diene and triethylamine in benzene at 80 °C. It appears most likely, therefore, that the cycloadduct (**9a**) arises, as planned (Scheme 1), by capture of the selenoaldehyde (**1a**), formed from the selenenyl precursor and triethylamine. More direct evidence for the transient existence of the selenoaldehyde came from studies, discussed later, on the retro-Diels–Alder cleavage of bridged cycloadducts.

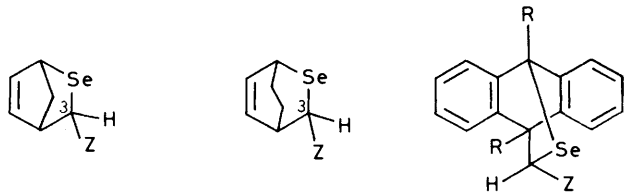
The stable, crystalline phthalimido derivative (**8a**) was chosen for experiments with a range of conjugated dienes. The corresponding sulphur derivative gave ethyl thioxoacetate cleanly in benzene at room temperature with only catalytic amounts of triethylamine.[3a] However, a higher reaction temperature again proved beneficial with the selenium derivative. Triethylamine (0.1 mol equiv.) in benzene was added slowly to the precursor (**8a**) (1 mol equiv.) and the diene (5 mol equiv.) in benzene with heating under reflux. The yields of isolated cycloadducts are given in the Table. Sauer *et al.*[9] have shown that 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. The yields of the corresponding selenoaldehyde adducts are therefore consistent with the trapping of a labile, electrophilic dienophile. In particular, the 64% yield (after purification) of the cyclopentadiene adducts (**12a**) and (**13a**) implies efficient generation of ethyl selenoxoacetate (**1a**) although effective trapping of this selenoaldehyde requires an excess of the most reactive diene. In contrast, ethyl thioxoacetate, generated from the corresponding thiophthalimide (**8a**; Se = S), was trapped essentially quantitatively with only one equivalent of cyclopentadiene at room temperature.[3a] The generally beneficial effect of heating on the yields of cycloadducts, even when the most reactive precursors, the selenenyl chloride and selenosulphonate, are used, is not understood. A similar effect was noted[2] on the yield of the thioaldehyde–anthracene adduct (**16**; Se = S), formed from the corresponding sulphenyl chloride. Possibly, the rates of cycloaddition increase with temperature

* The selenocyanate (**3a**) and the phthalimido derivative (**8a**) did not react with dimethylbutadiene in benzene at 80 °C.

Table. Cycloadducts[a] of conjugated dienes with ethyl selenoxoacetate (**1a**) formed[b] from the phthalimido precursor (**8a**)

Diene	Cycloadduct	Yield (%)
Cyclopentadiene	(**12a**) + (**13a**) (*ca.* 1:1)	64
2,3-Dimethylbuta-1,3-diene	(**9a**)[c]	54
Cyclohexa-1,3-diene	(**14a**) + (**15a**) (*ca.* 8:2)	26
Anthracene	(**16a**)	32

[a] See the text for the preparation of these cycloadducts from other precursors and for the preparation of the cycloadducts (**16a**), (**17a**), (**28a**), and (**29a**). [b] *Conditions*: Et_3N (0.1 mol equiv.) added to (**8a**) (1 mol equiv.) and the diene (5 mol equiv.) in benzene at 80 °C. [c] Similarly (**9b**), 45%.

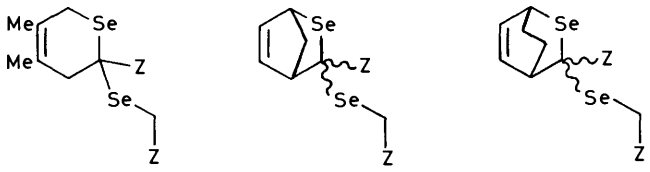


(**12**) *endo*-Z (**14**) *endo*-Z (**16**) R = H
(**13**) *exo* -Z (**15**) *exo* -Z (**17**) R = Me

more rapidly than those of competing reactions, such as polymerisation, of the seleno- and thio-aldehydes. Alternatively, more rapid elimination and cycloaddition, in conjunction with slow addition of reactants, may prevent an increase in the concentration of the reactive intermediates to levels where polymerisation predominates.

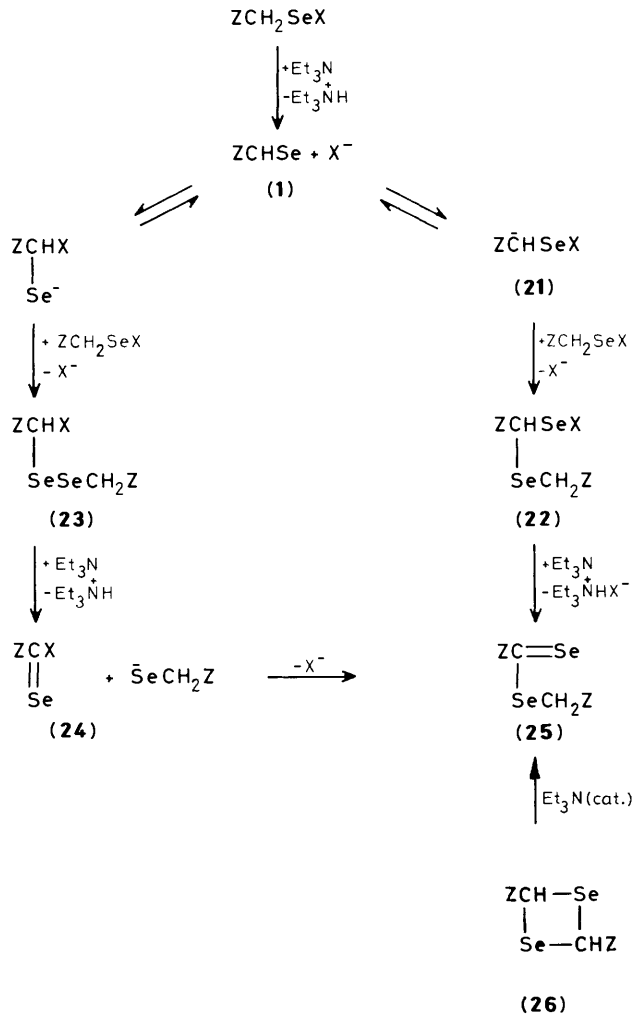
The structures of the cycloadducts were determined from their spectra, which were, as expected, closely similar to those of the corresponding thioaldehydes.[2,3] Additionally, the isotopic pattern of selenium aided interpretation of the mass spectra. Further, it was often possible, especially at high field, to detect satellites arising from ^{77}Se (7.6% natural abundance) in the ^1H and, occasionally, the ^{13}C n.m.r. spectra. For example, the signal for 2-H in the spectrum (360 MHz) of the adduct (**9a**), δ 3.81 (dd, *J* 8.5 and 4.9 Hz), was accompanied by a weak pair of corresponding double doublets, $^2J_{HSe}$ 13.3 Hz. The oily esters (**9a**) and (**9b**) were hydrolysed to give the same, crystalline acid (**9**; Z = CO_2H) as further confirmation of their structure.

Cycloadducts of Diselenoesters.—In experiments with the phthalimido (**8a**) and, especially, the selenocyanate (**3a**) precursors, the cycloadducts of dimethylbutadiene (**9a**), cyclopentadiene (**12a**) and (**13a**), and cyclohexadiene (**14a**) and (**15a**), were accompanied by diseleno derivatives, *viz.* (**18a**), (**19a**), and (**20a**). Products of this unexpected type were not observed when the selenosulphate (**4a**), selenenyl chloride (**6a**), or selenosulphonate (**7a**) precursors were employed; nor were



(**18**) (**19**) (**20**)

diseleno derivatives of anthracene, 9,10-dimethylanthracene, or thebaine (**27**) formed in any experiments. For example, slow addition of triethylamine to the selenocyanate (**3a**), dimethylbutadiene (5 mol equiv.), and calcium chloride in refluxing ethanol gave the cycloadduct (**9a**) (30%) and the diseleno derivative (**18a**) (19%). Again, the cycloadduct (**9a**), when prepared from the phthalimido precursor (**8a**) in benzene (see the Table), was accompanied by (**18a**) (13%). To test whether this second product was derived from the first by selenenylation, the adduct (**9a**) was heated with the precursor (**8a**) and triethylamine in benzene under the usual conditions. The cycloadduct (**9a**) was recovered from the mixture and no diseleno compound (**18a**) was detected. It appears therefore that the diseleno compounds (**18a**), (**19a**), and (**20a**), and those [(**18b**), (**18c**), and (**18e**)] accompanying the cycloadducts of other selenoaldehydes are derived by the trapping of diselenoesters, $ZCH_2SeC(=Se)Z$ (**25**) (Scheme 3). The yields of



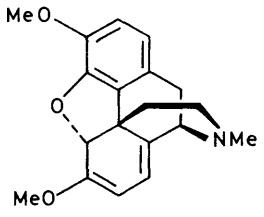
Scheme 3.

these diseleno adducts varied with the solvent and mode of addition of reactants, but no simple pattern emerged to clarify the mechanism of diselenoester formation.* Base-catalysed α-selenenylation of the precursor, ZCH_2SeX, to give the derivative (**22**) (Scheme 3) seems unlikely in view of the failure of the cycloadduct (**9a**) to undergo selenenylation. An indirect route to this intermediate (**22**) might involve formation of the carbanion

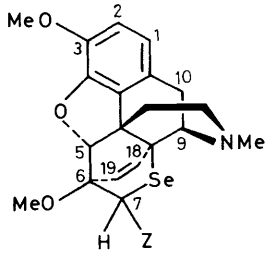
* Cycloadducts of $EtO_2CCH_2SC(=S)CO_2Et$ and 2,3-dimethylbuta-1,3-diene and cyclopentadiene are formed, along with the normal thioaldehyde adducts, from the phthalimido precursor (**8a**; Se = S) and triethylamine, but only in the presence of 4-dimethylaminopyridine.[10]

(**21**) from nucleophilic attack by X^- (alternatively, Et_3N may replace X^- as a nucleophile in Scheme 3) on the selenoaldehyde. Thiophilic attack by nucleophiles on thioxo compounds is known and similar attack on selenium would be assisted by the electron-withdrawing group Z. Alternatively, nucleophilic attack on carbon could lead to the diselenide (**23**) and thence, *via* the selenoxo derivative (**24**), to the diselenoester (**25**). A possible third route involves base-catalysed ring-opening of the selenoaldehyde dimer (**26**).

Relative Stereoselectivity of Seleno- and Thio-aldehydes.—Ethyl selenoxoacetate (**1a**), generated from the phthalimido precursor (**8a**), reacted at 80 °C with cyclopentadiene (see the Table) to give (64%) approximately equal amounts of the *endo*-(**12**) and *exo*-cycloadduct (**13**), which were separated chromatographically. The ratio was unchanged when the cycloadducts were prepared at room temperature, although the yield (24%) was diminished. Essentially the same ratio (*ca.* 1:1) was obtained using the selenosulphonate (**7a**), in ethanol or benzene. In contrast, ethyl thioxoacetate, like many common dienophiles, gave[3b] mixtures rich in the *endo*-isomer (*endo*:*exo* ratio, 7:3). The ratio obtained with the selenoaldehyde was shown to be kinetically determined by appropriate control experiments. Thus, each isomeric adduct was heated in benzene containing triethylamine (1 mol equiv.) to test whether epimerisation at C-3 or dissociation–recombination occurs under the conditions of synthesis. The adducts were unchanged. However, when the *endo*-adduct (**12**) was heated under reflux in toluene for 10 h, or the *exo*-adduct (**13**) for 7 h, an equilibrium mixture rich in the *exo*-isomer was obtained (*endo*:*exo* ratio, 3:7). In *this* respect, the selenoaldehyde adducts behave like those of the corresponding thioaldehyde (*endo*:*exo* ratio at equilibrium, 3:7) and other, common dienophiles. Another difference in stereoselectivity under conditions of kinetic control was observed in the reactions of ethyl selenoxo- and thioxo-acetate with the unsymmetrical diene, thebaine. Treatment of thebaine (**27**) with equimolar amounts of the selenosulphonate (**7a**), triethylamine, and calcium chloride in ethanol, as described before for dimethylbutadiene, gave a mixture (41%) of the cycloadducts (**28**) and (**29**) (ratio, 54:46), containing no substantial amounts



(**27**)



(**28**) 7α, ---Z
(**29**) 7β, —Z

of any 7-selena-8-ethoxycarbonyl isomer. The same ratio (*ca.* 1:1) was obtained with the phthalimido precursor (**8a**). Again, the stereoisomers (**28**) and (**29**) were unchanged when heated with triethylamine under the conditions of their formation. Ethyl thioxoacetate, in contrast, reacts with thebaine to give mainly[2] the *endo*-isomer (**28**; Se = S) (*ca.* 80%) together with[11] the *exo*-isomer (**29**; Se = S) (5—10%) and the 7-thia-8α-ethoxycarbonyl derivative (5—10%). A similar, but smaller, reduction in the stereoselectivity of ethyl selenoxoacetate relative to that of ethyl thioxoacetate was observed with cyclohexa-1,3-diene. The selenoaldehyde adducts (**14**) and (**15**) were formed in an *endo*:*exo* ratio (77:23) smaller than that for the corresponding thioaldehyde adducts (88:12). Thus, in reactions with 3 dienes the selenoaldehyde is less stereoselective than the thioaldehyde. This may reflect a greater reactivity, with an earlier, reactant-like transition state resulting in smaller secondary orbital (*endo*) interactions. Again, the longer C–Se *vs.* C–S bond length might lead to the same result.

Selenoaldehydes (**1**) *with Other Groups, Z.*—A limited set of other selenoaldehydes, a ketone (**1c**), an amide (**1d**), and a nitrile (**1e**), was studied to explore the scope of the synthetic method (Scheme 1) and provide a wider range of cycloadducts. The most conveniently prepared precursors were the selenocyanate (**3c**) and the selenosulphates (**4d**) and (**4e**). As usual, each precursor was heated under reflux with 2,3-dimethylbuta-1,3-diene (5 mol equiv.), in ethanol containing calcium chloride, and treated slowly with triethylamine. The resulting selenoaldehyde adducts (**9c**) [accompanied by (**18c**)], (**9d**), and (**9e**) [accompanied by (**18e**)] were isolated in 33, 32, and 40% yield, respectively. The yields are lower than those that might have been obtained using the phthalimido or selenosulphonate precursors. However, the selenocyanates and selenosulphates are available in one step from the alkyl halides. If good yields *based upon the dienes* are required then the use of cyclopentadiene or anthracene derivatives, described in the following section, is recommended. With this end in mind, we prepared the cycloadducts (**17c**) and (**17e**) of 9,10-dimethylanthracene. The yields, 13 and 25% respectively, were low despite the high reactivity of dimethylanthracene, but the conditions were not optimised and only 1 mol equivalent of the 'expensive' trapping agent was used.

Formation of Selenoaldehydes by Retro-Diels–Alder Reactions.—The foregoing, thermal equilibration of the *endo*-(**12a**) and *exo*-adduct (**13a**) of ethyl selenoxoacetate (**1a**) showed that these cycloadducts, like those of ethyl thioxoacetate, dissociate reversibly at experimentally convenient temperatures. We expected them, therefore, to release the selenoaldehyde for trapping *in situ* by another diene. Accordingly, the 'kinetic' mixture (1:1) of the cyclopentadiene adducts (**12a**) and (**13a**) was heated with 2,3-dimethylbuta-1,3-diene (1.1 mol equiv.) in toluene in a sealed tube at 100 °C for 21 h. Evaporation of the mixture gave the adduct (**9a**) in an essentially pure state (85% after distillation). The anthracene adduct (**16a**), more conveniently prepared (28%) from anthracene (5 mol equiv.) with the selenenyl chloride (**6a**), rather than with the phthalimido derivative (**8a**), was expected to behave similarly. Indeed, heating in toluene with dimethylbutadiene (1.1 mol equiv.) at 120 °C for 5 h, or 80 °C for 64 h, gave the selenine (**9a**) (87%) and anthracene. In several trial experiments, the thioaldehyde (**16a**; Se = S) and selenoaldehyde adduct (**16a**) of anthracene appeared (t.l.c. control) to dissociate in the presence of various conjugated dienes at similar rates. A quantitative experiment confirmed this. Equimolar amounts of the adducts (**16a**; Se = S) and (**16a**), and dimethylbutadiene were heated in benzene for 5 h to afford the thioaldehyde (**9a**; Se = S) and selenoaldehyde adduct (**9a**) in the ratio 58:42 (measured by ^1H n.m.r. spectroscopy) and a combined yield of 64% (after isolation).

Earlier experience with cycloadducts of 9,10-dimethylanthracene suggested that those of the selenoaldehydes (**17**) might be formed in better yield than the anthracene adducts (**16**) (9,10-dimethylanthracene reacts faster than anthracene with maleic anhydride)[9] yet might likewise dissociate at convenient rates. Indeed, the dimethylanthracene adduct (**17a**), prepared in 61% yield from the selenenyl chloride (**6a**) and dimethylanthracene (1 mol equiv.), reacted faster than its anthracene analogue (**16a**) with dimethylbutadiene. When equimolar amounts of each adduct and dimethylbutadiene were heated separately under reflux in benzene, transfer of the selenoaldehyde from the dimethylanthracene adduct had proceeded by 40% and

from the anthracene adduct by only 5% after 1 h. As expected, heating the dimethylanthracene adduct (**17a**) alone with dimethylbutadiene (1 mol equiv.) for 2 h at 120 °C in toluene gave a high yield (96%) of the selenine (**9a**). Similarly, when the phenacyl- (**17a**) and cyano-selenoaldehyde adduct (**17e**) were separately heated in benzene in a sealed tube at 110—120 °C for 5 h with dimethylbutadiene, high yields of the corresponding selenines (**9c**) (91%) and (**9e**) (88%) were obtained.

Summary and Discussion of Related Investigations.—To summarise, 5 classes of selenenyl derivatives have been identified that undergo elimination with triethylamine to form transient selenoaldehydes. They do so efficiently, as judged by the yields of cyclopentadiene and 9,10-dimethylanthracene adducts. In all cases an electron-withdrawing group, either an ester, a keto, an amido, or a cyano group, assists elimination and, if the analogy with thioaldehyde synthesis holds, may be necessary for this purpose, especially with the 'seleno Bunte salts' (**4**). However, elimination of cyanide from the selenocyanates (**3**) occurs readily unlike that from thiocyanates, and the range of possible Z and X groups merits further study. The selenocyanates (**3**) and selenosulphates (**4**) are the most readily prepared from selenium-free starting materials (**2**), but are not necessarily the best precursors of selenoaldehydes. Efficient trapping of selenoaldehydes under the conditions of their formation from the selenenyl precursors is generally more difficult than for thioaldehydes. Also, in certain cases the cycloadducts are accompanied by adducts of diselenoesters. For these reasons the cyclopentadiene, anthracene, and 9,10-dimethylanthracene adducts are recommended as ancillary precursors, especially for the synthesis of the cycloadducts of simple selenoaldehydes and complex, 'expensive' dienes. Further, the essentially quantitative thermal transfer of selenoaldehydes from these bridged cycloadducts to 2,3-dimethylbuta-1,3-diene provides compelling evidence for the independent existence of this neglected class of reactive intermediates. The stable, crystalline anthracene and dimethylanthracene adducts should enable further exploration of selenoaldehyde chemistry under controlled conditions. Moreover, chemical modification of the adducts should provide precursors for the generation of new selenoxo derivatives by retro-Diels–Alder reactions.

Until very recently[12] the chemistry of selenoaldehydes has been largely unexplored. Even selenoketones (selones) were neglected until the work of Barton *et al.*[13] The discovery[1] of electronically stabilised selenoaldehydes was followed by gas-phase, spectroscopic studies on selenoacetaldehyde and selenoformaldehyde and on the preparation of metal complexes of the latter.[14] Recently, Fischer *et al.*[15] 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. While the present work was in progress,[16] Krafft and Meinke reported[12] the preparation of simple selenoaldehydes from α-(phenyldimethylsilyl)selenocyanates by cleavage with tetrabutylammonium fluoride. The selenoaldehydes were trapped *in situ* at 0 °C with cyclopentadiene (2 mol equiv.), generally in good yield. Slow addition of the quaternary ammonium fluoride was employed to suppress polymerisation of the selenoaldehydes. Interestingly, *endo*-rich mixtures of cyclopentadiene adducts were obtained even though the selenoaldehydes, RCHSe, had simple alkyl and aryl substituents, R, for example Me, Et, and Ph.[17] Perhaps these selenoaldehydes, RCHSe, are less reactive and consequently more stereoselective than those, ZCHSe, described in this paper. In accord with this, the highest *endo*:*exo* ratio (9.0:1), and lowest yield (39%), were recorded[12] for the adducts of the most hindered dienophile, Bu^{t}CHSe, and the lowest *endo*:*exo* ratio (2.3:1) (83% yield) for the least hindered dienophile, MeCHSe.*

Experimental

General Methods.—Except where otherwise stated, i.r. spectra were recorded for KBr discs, n.m.r. spectra for deuteriochloroform solutions with tetramethylsilane as an internal standard at 90 MHz for ^1H and 25.2 MHz for ^{13}C, and light petroleum refers to the fraction b.p. 40—60 °C. Mass spectra were obtained by electron impact with an ionising voltage of 70 eV. The composition of selenium derivatives was verified routinely by the selenium isotopic patterns of low resolution mass spectra (MS 12 spectrometer), but data are recorded only for critical, accurate mass measurements (MS 9 spectrometer). Solutions in organic solvents were dried over $MgSO_4$. Solvents were evaporated throughout under reduced pressure. High-boiling liquids were purified by Kugelrohr distillation; the cited 'b.p.' is the oven temperature not the equilibrium b.p.

Chromatographic Purification of Cycloadducts.—Cycloadducts (**9**) of dimethylbutadiene were purified on Merck silica GF_{254} plates developed with ether–light petroleum (3:7). They generally gave higher R_F values (0.5—0.8) than the corresponding diselenoester adducts (**18**) (0.4—0.6). Exceptionally, the polar adduct (**9d**) was chromatographed (R_F 0.27) with ether–light petroleum (1:1). Cycloadducts of cyclopentadiene (**12**) and (**13**) and cyclohexadiene (**14**) and (**15**) were initially obtained chromatographically as mixtures, as described for the adducts (**9**). Separation of the *endo*- and *exo*-isomers was achieved by multiple development of silica plates with ether–light petroleum (1:9); generally, the *endo*-isomers gave the higher R_F values. Cycloadducts of anthracene (**16**) and dimethylanthracene (**17**) were purified on a short column of t.l.c. grade silica eluted with batches of light petroleum containing increasing quantities (5—50%) of chloroform. Occasionally, further purification by t.l.c., as described for the adducts (**9**), was required. Alternatively, separation of anthracene and dimethylanthracene from the corresponding cycloadducts was effected on silica plates developed with benzene. Final purification was then achieved as described for the adducts (**9**). Mixtures containing the cycloadducts (**28**) and (**29**) and the more polar thebaine (**27**) were readily separated on silica plates, as described for (**9**).

Presentation of Experimental Procedures.—The preparations of reactants and products are presented in the following order. *Selenoaldehyde precursors* (Scheme 2): (**3a**), (**3c**), (**4a**), (**4b**), (**4d**), (**4e**), (**5a**), (**5b**), (**6a**), (**6b**), (**7a**), (**8a**), and (**8b**); *cycloadducts of dimethylbutadiene*: (**9a**), (**9**; Z = CO_2H), (**18a**), (**18**; Z = CO_2H), (**9b**), (**18b**), (**9c**), (**18c**), (**9d**), (**9e**), and (**18e**); *cycloadducts of cyclopentadiene*: (**12a**), (**13a**), and (**19a**); *cycloadducts of cyclohexadiene*: (**14a**), (**15a**), and (**20a**); *cycloadducts of anthracene*: (**16a**) and (**16**; Z = CO_2H); *cycloadducts of dimethylanthracene*: (**17a**), (**17c**), and (**17e**); *cycloadducts of thebaine* (**27**), (**28**), and (**29**); 1,2- *and* 1,4-*adducts of dimethylbutadiene*: (**10**; X = EtO), (**11**; X = 4-$MeC_6H_4SO_2$), (**10**; X = Cl), and (**11**; X = Cl). There then follow *retro-Diels–Alder reactions of* (**12a**), (**13a**), (**16a**), (**16a**; Se = S), (**17c**), (**17e**), and (**17a**). Various control experiments are described in adequate detail in the main text.

Ethoxycarbonylmethyl Selenocyanate (**3a**).—Ethyl bromoacetate (5.00 g, 0.030 mol) and potassium selenocyanate (5.05 g, 0.035 mol) were heated under reflux in ethanol (100 ml) for 1 h. The mixture was cooled and filtered to remove potassium bromide. The filtrate was evaporated and the residual oil was distilled to give *ethoxycarbonylmethyl selenocyanate* (**3a**) (3.72 g,

* *Note added in proof:* see p. 1922.

65%), b.p. 72—78 °C (0.25 mmHg) (Found: C, 31.3; H, 3.65; N, 7.4. $C_5H_7NO_2Se$ requires C, 31.3; H, 3.7; N, 7.3%); $\nu_{max.}$(liquid film) 2 160 and 1 735 cm^{-1}; δ_H 1.28 (t, *J* 7 Hz, Me), 3.83 (s, with ^{77}Se satellites, J_{HSe} 16 Hz, $SeCH_2$) and 4.27 (q, *J* 7 Hz, OCH_2); δ_C 14.0 (Me), 28.1 ($SeCH_2$), 62.8 (OCH_2), 100.3 (CN), and 167.5 (CO_2Et).

Benzoylmethyl Selenocyanate (**3c**).—This was prepared as described by Thorstenson and Songstad[8] from phenacyl bromide and potassium selenocyanate in ethanol at room temperature. The selenocyanate (**3c**) (66%) had m.p. 88 °C (from diethyl ether) (lit.,[8] 88 °C); $\nu_{max.}$ 2 160 and 1 665 cm^{-1}; δ_H 4.88 (s, with ^{77}Se satellites, J_{HSe} 18 Hz, $SeCH_2$), 7.50 (3 H, m, *m*- and *p*-phenyl-H), and 7.95 (2 H, *o*-phenyl-H).

Potassium Se-*Ethoxycarbonyl- and* Se-*Methoxycarbonylmethyl Selenosulphate* (**4a**) *and* (**4b**).—Powdered selenium (13.8 g, 0.175 mol) and potassium sulphite (36 g, 0.23 mol) were heated under reflux in water (200 ml) for 50 min to form potassium selenosulphate.[4] The mixture was filtered and either ethyl bromoacetate (29 g, 0.174 mol) in ethanol (50 ml), or methyl bromoacetate (26.6 g, 0.174 mol) in methanol (50 ml), was added to the hot filtrate. The mixtures were heated under reflux for 15 min and then evaporated. The white residues were extracted with either hot ethanol, for (**4a**), or hot methanol, for (**4b**). The extracts yielded *potassium* Se-*ethoxycarbonylmethyl selenosulphate* (**4a**) (35.6 g, 72%), m.p. 143—147 °C (from ethanol) (Found: C, 17.1; H, 2.4; S, 11.5. $C_4H_7KO_5SSe$ requires C, 16.8; H, 2.5; S, 11.2%); $\nu_{max.}$ 1 725 cm^{-1}; δ_H(D_2O; standard: Bu^tOH, δ 1.28) 1.33 (t, *J* 7 Hz, Me), 4.01 (s, with ^{77}Se satellites, J_{HSe} 13 Hz, $SeCH_2$), and 4.28 (q, *J* 7 Hz, OCH_2); δ_C(solvent, D_2O; standard: dioxane, δ 67.4) 14.1 (Me), 30.9 ($SeCH_2$), 63.7 (OCH_2), and 173.55 (CO_2Et); and *potassium* Se-*methoxycarbonylmethyl selenosulphate* (**4b**) (27.1 g, 57%), m.p. 154—157 °C (decomp.) (from methanol) (Found: C, 13.3; H, 1.7; S, 11.6. $C_3H_5O_5KSSe$ requires C, 13.3; H, 1.9; S, 11.8%); $\nu_{max.}$ 1 725 cm^{-1}; δ_H(D_2O; standard: Bu^tOH, δ 1.28) 3.80 (s, Me) and 3.98 (s, with ^{77}Se satellites, J_{HSe} 12 Hz, $SeCH_2$); δ_C(D_2O; standard: dioxane, δ 67.4) 30.8 (CH_2), 54.3 (Me), and 174.0 (CO_2Me).

Potassium Se-*Phenylaminocarbonylmethyl Selenosulphate* (**4d**).—Aqueous potassium selenosulphate, prepared from selenium and potassium sulphite as described for (**4a**), and ethanolic *N*-phenyl-2-bromoacetamide were heated under reflux to give, after the usual work-up, *potassium* Se-*phenylaminocarbonylmethyl selenosulphate* (**4d**) (30%), m.p. 159—163 °C (decomp.) (from ethanol) (Found: C, 29.2; H, 2.3; N, 4.2. $C_8H_8KNO_4SSe$ requires C, 28.9; H, 2.4; N, 4.2%); $\nu_{max.}$ 3 300 and 1 660 cm^{-1}; δ_H(D_2O; standard: Bu^tOH, δ 1.28) 4.04 (s, $SeCH_2$) and 7.51 (m, Ph); δ_C(D_2O; standard: dioxane, δ 67.4) 34.4 ($SeCH_2$), 121.9, 126.2, 130.2 and 138.4 (Ph), and 170.8 (CO).

Potassium Se-*Cyanomethyl Selenosulphate* (**4e**).—Chloroacetonitrile and potassium selenosulphate in aqueous ethanol gave, as described for the preparation of (**4a**), *potassium* Se-*cyanomethyl selenosulphate* (**4e**) (48%), m.p. 129—133 °C (from methanol) (Found: C, 10.4; H, 0.3; N, 6.0. $C_2H_2KNO_3SSe$ requires C, 10.1; H, 0.85; N, 5.9%); $\nu_{max.}$ 2 240 cm^{-1}; δ_H(D_2O; standard: Bu^tOH, δ 1.28) 4.03 (s, with ^{77}Se satellites, J_{HSe} 15 Hz, CH_2); δ_C(D_2O; standard: dioxane, δ 67.4) 10.8 (CH_2) and 120.6 (CN).

Di(ethoxycarbonylmethyl) and Di(methoxycarbonylmethyl) Diselenide (**5a**) *and* (**5b**).—The selenosulphate (**4a**) (19 g, 0.066 mol) or (**4b**) (18 g, 0.066 mol) in water (100 ml) at 0 °C was treated dropwise with stirring with iodine (8.7 g, 0.070 mol) in ethanol or methanol, respectively. The mixture was allowed to warm to room temperature before being treated with aqueous sulphur dioxide to destroy any excess of iodine. The mixture was made alkaline with saturated aqueous sodium hydrogen carbonate and was then concentrated to remove ethanol or methanol. Extraction with dichloromethane gave *di(ethoxycarbonylmethyl) diselenide* (**5a**) (8.7 g, 79%), b.p. 86—90 °C (0.2 mmHg, Kugelrohr distillation) (Found: C, 28.8; H, 4.0. $C_8H_{14}O_4Se_2$ requires C, 28.9; H, 4.3%); $\nu_{max.}$(liquid film) 1 730 cm^{-1}; δ_H 1.27 (t, *J* 7 Hz, Me), 3.73 (s, with ^{77}Se satellites, J_{HSe} 16 Hz, $SeCH_2$), and 4.20 (q, *J* 7 Hz, OCH_2); δ_C 14.1 (Me), 29.5 ($SeCH_2$), 61.3 (OCH_2), and 170.3 (CO_2Et), or *di(methoxycarbonylmethyl) diselenide* (**5b**) (5.23 g, 52%), b.p. 160—165 °C (0.7 mmHg, Kugelrohr distillation) (Found: C, 23.6; H, 3.4. $C_6H_{10}O_4Se_2$ requires C, 23.7; H, 3.3%); $\nu_{max.}$(liquid film) 1 730 cm^{-1}; δ_H 3.73 (s, CO_2Me, and $SeCH_2$ with ^{77}Se satellites, J_{HSe} 16 Hz); δ_C 28.9 ($SeCH_2$, with ^{77}Se satellites, J_{CSe} 49 Hz), 52.4 (Me), and 170.8 (CO_2Me).

Ethoxycarbonyl- and Methoxycarbonyl-methylselenenyl Chloride (**6a**) *and* (**6b**).—Freshly distilled sulphuryl chloride (43.2 mg, 0.32 mmol) in benzene (10 ml) was added slowly to the diselenide (**6a**) (106 mg, 0.32 mmol) or (**6b**) (97 mg, 0.32 mmol) in benzene (20 ml) at room temperature with the exclusion of direct sunlight. The mixture was kept for 1 h then evaporated at near room temperature to give the ethyl ester (**6a**); δ_H 1.27 (t, *J* 7 Hz, Me), 4.22 (s, $SeCH_2$), and 4.25 (q, *J* 7 Hz, OCH_2), or the methyl ester (**6b**); δ_H(CCl_4) 3.75 (s, OMe) and 4.20 (s, $SeCH_2$). Both selenenyl chlorides were obtained as dark red oils and were dissolved in appropriate solvents for immediate use.

Se-*Ethoxycarbonylmethyl Toluene*-4-*selenosulphonate* (**7a**).—The selenenyl chloride (**6a**) (6.0 mmol) in benzene (25 ml) was added dropwise with stirring to sodium toluene-4-sulphinate tetrahydrate (6.4 mmol) in ethanol (50 ml) and benzene (50 ml) at 0 °C. The deep red colour of the selenenyl chloride was rapidly discharged. After 15 min the mixture was evaporated and the residue was stirred with ether and the resulting suspension was filtered. The filtrate was dried and evaporated to give the *selenosulphonate* (**7a**) (1.79 g, 93%) as an oil that decomposed upon attempted distillation (Found: M^+, 321.9783. $C_{11}H_{14}O_4S^{80}Se$ requires *M*, 321.9964); $\nu_{max.}$(liquid film) 1 730 cm^{-1}; δ_H 1.17 (t, *J* 7 Hz, $OCH_2\mathit{Me}$), 2.45 (s, Ar*Me*), 3.93 (s, $SeCH_2$), 4.10 (q, *J* 7 Hz, OCH_2), 7.35 (d, *J* 9 Hz, 3,5-ArH), and 7.78 (d, *J* 9 Hz, 2,6-ArH); δ_C 13.9 ($OCH_2\mathit{Me}$), 21.5 (Ar*Me*), 32.5 ($SeCH_2$), 62.0 (OCH_2), 126.6, 129.8, 144.0, and 145.1 (Ar), and 168.2 (CO_2Et).

N-(*Ethoxycarbonylmethylseleno*)- *and* N-(*Methoxycarbonyl methylseleno*)-*phthalimide* (**8a**) *and* (**8b**).—Freshly prepared, powdered potassium phthalimide (20 mmol) was added, with stirring, to the appropriate selenenyl chloride (**6a**) or (**6b**) (18 mmol) in dry 1,2-dichloroethane (50 ml) at 0 °C.[7] After 10 min the colour of the mixture had faded from dark red to pale yellow. The mixture was filtered and the filtrate was evaporated to low volume (*ca.* 5 ml) and diluted with hexane (100 ml) to precipitate the required product. The *ethyl ester* (**8a**) (2.34 g, 42%) had m.p. 111—114 °C (from hexane) (Found: C, 46.5; H, 3.4; N, 4.5. $C_{12}H_{11}NO_4Se$ requires C, 46.2; H, 3.5; N, 4.5%); $\nu_{max.}$ 1 775 and 1 750 cm^{-1}; δ_H 1.16 (t, *J* 7 Hz, Me), 3.72 (s, with ^{77}Se satellites, J_{HSe} 18 Hz, $SeCH_2$), 4.14 (q, *J* 7 Hz, OCH_2), and 7.6—8.0 (m, ArH); δ_C 13.75 (Me), 31.5 ($SeCH_2$), 61.9 (OCH_2), 123.8, 132.6, and 134.3 (Ar), and 168.9 and 169.3 (CO). The *methyl ester* (**8b**) (1.97 g, 37%) had m.p. 147—153 °C (decomp.) (from benzene) (Found: C, 44.6; H, 3.0; N, 4.7. $C_{11}H_9NO_4Se$ requires C, 44.3; H, 3.0; N, 4.7%); $\nu_{max.}$ 1 770, 1 750, 1 740, 1 720, and 1 700 cm^{-1}; δ_H 3.65 (s, Me), 3.68 (s, with ^{77}Se satellites, J_{HSe} 18 Hz, $SeCH_2$), and 7.6—8.0 (m, ArH); δ_C 31.2 ($SeCH_2$), 52.9 (OMe), 123.8, 132.55, and 134.4 (Ar), and 169.0 and 169.8 (CO).

Cycloadduct (**9a**) *of* 2,3-*Dimethylbuta*-1,3-*diene and Ethyl Selenoxoacetate* (**1a**) *and the Corresponding Carboxylic Acid* (**9**; Z = CO_2H): *Preparation from the Toluene*-4-*selenosulphonate* (**7a**).—The toluene-4-selenosulphonate (**7a**) (251 mg, 0.78 mmol) in ethanol (5 ml) was added slowly during 15 min to 2,3-dimethylbuta-1,3-diene (320 mg, 3.9 mmol), calcium chloride dihydrate (117 mg, 0.80 mmol), and triethylamine (80 mg, 0.79 mmol) in ethanol (25 ml) with heating under reflux. The mixture was heated for a further 15 min, was then cooled, diluted with chloroform (100 ml), and filtered through Celite. The filtrate was evaporated and the residue was treated with aqueous sodium hydrogen carbonate and dichloromethane. The organic layer was dried and evaporated to give *ethyl* 3,6-*dihydro*-4,5-*dimethyl*-2H-*selenine*-2-*carboxylate* (**9a**) which, after chromatography (see the General Methods section) was obtained as an oil (113 mg, 59%), b.p. 120—123 °C (0.035 mmHg, Kugelrohr distillation) [Found: C, 48.4; H, 6.4%; M^+, 248.0328. $C_{10}H_{16}O_2Se$ requires C, 48.6; H, 6.5%; M (^{80}Se), 248.0315]; $\nu_{max.}$ 1 725 cm^{-1}; δ_H 1.25 (t, J 7 Hz, OCH_2Me), 1.79 (br s, 4- and 5-Me), 2.52 (m, 3-H_2), 3.14 (m, 6-H_2), 3.81 [dd, J 8.5 and 4.9 Hz, with ^{77}Se satellites (360 MHz spectrum), J_{HSe} 13.3 Hz], and 4.17 (q, J 7 Hz, OCH_2); δ_C 14.1 (OCH_2Me), 19.3 and 20.3 (4- and 5-Me), 22.7 (C-6), 34.4 (C-3), 35.6 (C-2), 61.05 (OCH_2), 126.6 and 129.0 (C-4 and -5), and 173.3 (CO_2Et). The ester (**9a**) (0.3 g) was hydrolysed at room temperature for 24 h in ethanol (1 ml) and water (10 ml) containing sodium hydroxide (0.1 g) to give 3,6-*dihydro*-4,5-*dimethyl*-2H-*selenine*-2-*carboxylic acid* (**9**; Z = CO_2H), m.p. 85—86 °C [from light petroleum (b.p. 60—80 °C)] (Found: C, 44.0; H, 5.5. $C_8H_{12}O_2Se$ requires C, 43.8; H, 5.5%); $\nu_{max.}$ 1 697 cm^{-1}; δ_H 1.81 (br s, 4- and 5-Me), 2.47 (m, 3-H_2), 3.14 (m, 6-H_2), 3.81 (t, J 7 Hz, 2-H), 9.4 (br s, OH, exch. with D_2O); δ_C 19.3 and 20.4 (4- and 5-Me), 22.7 (C-6), 33.9 (C-3), 35.2 (C-2), 126.8 and 128.8 (C-4 and -5), and 180.0 (CO_2H).

Preparation of (**9a**) *and the Diseleno Derivative* (**18a**) *and the Corresponding Dicarboxylic Acid* (**18**; Z = CO_2H) *from the Selenocyanate* (**3a**).—Triethylamine (0.27 g, 2.6 mmol) in ethanol (5 ml) was added slowly during 15 min to the selenocyanate (**3a**) (0.5 g, 2.6 mmol), 2,3-dimethylbuta-1,3-diene (1.07 g, 13 mmol), and calcium chloride dihydrate (0.38 g, 2.6 mmol) in ethanol with heating under reflux. Heating was continued for 15 min and the mixture was then cooled, diluted with chloroform (100 ml), and filtered. The filtrate was evaporated and the residue was extracted with dichloromethane. The extract was washed with dilute hydrochloric acid and then with water and was dried and evaporated. Chromatography (see the General Methods section) of the residue gave the cycloadduct (**9a**) (193 mg, 30%) and *ethyl* 2-*ethoxycarbonylmethylseleno*-3,6-*dihydro*-4,5-*dimethyl*-2H-*selenine*-2-*carboxylate* (**18a**) (19%) as an oil that decomposed upon attempted distillation (Found: M^+, 409.9863. $C_{14}H_{22}O_4{}^{78}Se_2$ requires M, 409.9865); δ_H 1.23 and 1.27 (overlapping triplets, J 7 Hz, 2 × OCH_2Me), 1.80 (br s, 4- and 5-Me), 2.65 and 3.00 (AB system, J 16 Hz, 3-H_2), 3.15 (m. 6-H_2), 3.35 (s, with ^{77}Se satellites, J_{HSe} 13 Hz, $SeCH_2CO_2Et$), and 4.14 and 4.22 (2 × q, J 7 Hz, 2 × OCH_2Me). Hydrolysis of (**18a**), as described for (**9a**) gave 2-*carboxymethylseleno*-3,6-*dihydro*-4,5-*dimethyl*-2H-*selenine*-2-*carboxylic acid* (**18**; Z = CO_2H), m.p. 147—149 °C (from diethyl ether) (Found: C, 33.8; H, 4.1. $C_{10}H_{14}O_4Se_2$ requires C, 33.7; H, 4.0%); δ_H(CD_3OD) 1.82 (br s, 4- and 5-Me), 2.85 (m, 3-H_2), 3.30 (m, 6-H_2), and 3.37 (s, $SeCH_2CO_2D$).

Preparation of (**9a**) *from the Phthalimido Derivative* (**8a**).—Triethylamine (6.5 mg, 0.064 mmol) in benzene (10 ml) was added slowly during 15 min to the phthalimido derivative (**8a**) (0.20 g, 0.64 mmol) and 2,3-dimethylbuta-1,3-diene (0.26 g, 3.2 mmol) in benzene (20 ml) with heating under reflux. Heating was continued for 15 min and then the mixture was cooled and set aside to allow phthalimide to crystallise out. The mixture was filtered and the filtrate was evaporated. Chromatography of the residue gave the cycloadduct (**9a**) (85 mg, 54%) and a small quantity of the diseleno derivative (**18a**).

Preparation of (**9a**) *from the Selenenyl Chloride* (**6a**).—A freshly prepared solution of the selenenyl chloride (**6a**) 0.64 mmol) in benzene (10 ml) was added slowly over 15 min to 2,3-dimethylbuta-1,3-diene (263 mg, 3.2 mmol) and triethylamine (81.1 mg, 0.80 mmol) in benzene (10 ml) and ethanol (10 ml) with heating under reflux. The red colour of the selenenyl chloride was rapidly discharged and replaced by a yellow colour characteristic of the diselenide (**5a**). The mixture was heated for a further 15 min then was cooled, washed with aqueous sodium hydrogen carbonate then water, dried, and evaporated. Chromatography of the yellow, oily residue gave the cycloadduct (**9a**) (57 mg, 36%) and the diselenide (**5a**).

Preparation of (**9a**) *from the Selenosulphate* (**4a**).—Triethylamine (80 mg, 0.79 mmol) in ethanol (10 ml) was added slowly during 15 min to 2,3-dimethylbuta-1,3-diene (263 mg, 3.2 mmol), the selenosulphate (**4a**) (182 mg, 0.64 mmol), and calcium chloride dihydrate (118 mg, 0.80 mmol) in ethanol (30 ml) with heating under reflux. The mixture was heated for a further 15 min then was cooled and diluted with chloroform (100 ml). The mixture was filtered through Celite and the filtrate was evaporated. The residue, dissolved in dichloromethane, was washed with dilute hydrochloric acid then water. The solution was dried and evaporated. Chromatography of the residue gave the cycloadduct (**9a**) (47 mg, 30%) and a small amount of the diseleno derivative (**18a**).

Cycloadduct (**9b**) *of* 2,3-*Dimethylbuta*-1,3-*diene and Methyl Selenoxoacetate* (**1b**) *and the Corresponding Diseleno Derivative* (**18b**), *Prepared from the Phthalimido Derivative* (**8b**).—The phthalimido derivative (**8b**) (0.64 mmol), 2,3-dimethylbuta-1,3-diene (3.2 mmol), and triethylamine (0.064 mmol) gave, under the conditions described for the preparation of (**9a**), *methyl* 3,6-*dihydro*-4,5-*dimethyl*-2H-*selenine*-2-*carboxylate* (**9b**) (45%), b.p. 150—155 °C (0.8 mmHg, Kugelrohr distillation) (Found: C, 46.6; H, 6.1. $C_9H_{14}O_2Se$ requires C, 46.4; H, 6.1%); $\nu_{max.}$(liquid film) 1 735 cm^{-1}; δ_H 1.78 (br s, 4- and 5-Me), 2.50 (m, 3-H_2), 3.12 (br s, 6-H_2), 3.70 (s, OMe), and 3.81 (dd, J 5.5 and 7.5 Hz, 2-H); δ_C 19.3 and 20.4 (4- and 5-Me), 22.7 (C-6), 34.4 (C-3), 35.3 (C-2), 52.2 (OMe), 126.7 and 129.0 (C-4 and -5), and 173.7 (CO_2Me). Hydrolysis of (**9b**) gave the carboxylic acid (**9**; Z = CO_2H) obtained similarly from (**9a**). The ester (**9b**) was accompanied by the diseleno derivative (**18b**), δ_H 1.78 (br s, 4- and 5-Me), 2.80 (m, 3-H_2), 3.10 (m, 6-H_2), 3.36 (s, $SeCH_2CO_2Me$), and 3.70 (s, OMe). This diester was hydrolysed to give the diacid (**18**; Z = CO_2H) obtained similarly from (**18a**).

Cycloadduct (**9c**) *of* 2,3-*Dimethylbuta*-1,3-*diene and* 2-*Oxo*-2-*phenylethaneselenal* (**1c**) *and the Corresponding Diseleno Derivative* (**18c**), *Prepared from the Selenocyanate* (**3c**).—The selenocyanate (**3c**), 2,3-dimethylbuta-1,3-diene, calcium chloride, and triethylamine gave, as described for the cycloadduct (**9a**), 2-*benzoyl*-3,6-*dihydro*-4,5-*dimethyl*-2H-*selenine* (**9c**) (33%), b.p. 225 °C (0.04 mmHg, Kugelrohr distillation) (Found: C, 60.3; H, 5.5. $C_{14}H_{16}OSe$ requires C, 60.2; H, 5.8%); $\nu_{max.}$(liquid film) 1 680 cm^{-1}; δ_H 1.81 (br s, 4- and 5-Me), 2.55 (m, 3-H_2), 3.10 (m, 6-H_2), 4.65 (dd, J 5.5 and 8.0 Hz, 2-H), 7.45 (m, *m*- and *p*-ArH), and 7.93 (distorted dd, J 8.0 and 2.0 Hz, *o*-ArH); δ_C 19.3 and 20.3 (4- and 5-Me), 23.5 (C-6), 33.1 (C-3), 38.7 (C-2), 126.0 (C-4), 128.2 and 128.5 (Ph), 129.6 (C-5), 132.9 and 136.0 (Ph), and 196.5 (Ph*C*O). This cycloadduct was accompanied by the diseleno derivative (**18c**) (decomposed upon attempted distillation); δ_H

1.76 and 1.84 (4- and 5-Me), 2.95 (m, 3-H_2), 3.15 (m, 6-H_2), 3.90 (br s, SeCH_2COPh), and 7.1—8.2 (m, ArH).

Cycloadduct (**9d**) *of* 2,3-*Dimethylbuta*-1,3-*diene and* N-*Phenylselenoxoacetamide* (**1d**), *Prepared from the Selenosulphate* (**4d**).—The selenosulphate (**4d**), 2,3-dimethylbuta-1,3-diene, calcium chloride, and triethylamine gave, as described for the cycloadduct (**9a**), 3,6-*dihydro*-4,5-*dimethyl*-N-*phenyl*-2H-*selenine*-2-*carboxamide* (32%), m.p. 126—128 °C (from propan-2-ol–diethyl ether) (Found: C, 56.45; H, 5.8; N, 4.65. $C_{14}H_{17}NOSe$ requires C, 57.1; H, 5.8; N, 4.8%); $\nu_{max.}$ 3 260 and 1 652 cm^{-1}; δ_H 1.78 and 1.85 (s, 4- and 5-Me), 2.70 (m, 3-H_2), 3.20 (br s, 6-H_2), 3.99 (t, *J* 5.5 Hz, 2-H), 7.1—7.6 (m, Ph), and 8.4 (br s, exchanged with D_2O, NH); δ_C 19.2 and 20.5 (4- and 5-Me), 22.6 (C-6), 35.8 (C-3), 40.5 (C-2), 119.8, 124.4, and 128.9 (Ph), 126.7 and 129.6 (4- and 5-C), 137.9 (Ph), and 170.5 (PhNH*C*O).

Cycloadduct (**9e**) *of* 2,3-*Dimethylbuta*-1,3-*diene and Selenoxoacetonitrile* (**1e**), *and the Corresponding Diseleno Derivative* (**18e**), *Prepared from the Selenosulphate* (**4e**).—The selenosulphate (**4e**), 2,3-dimethylbuta-1,3-diene, calcium chloride, and triethylamine gave, as described for the cycloadduct (**9a**), 3,6-*dihydro*-4,5-*dimethyl*-2H-*selenine*-2-*carbonitrile* (**9e**) (40%), b.p. 145—150 °C (0.05 mmHg, Kugelrohr distillation) (Found: C, 48.15; H, 5.6; N, 6.9. $C_8H_{11}NSe$ requires C, 48.0; H, 5.5; N, 7.0%); $\nu_{max.}$(liquid film) 2 230 cm^{-1}; δ_H 1.78 and 1.82 (2 × s, 4- and 5-Me), 2.55 (m, 3-H_2), 3.15 and 3.45 (AB system, *J* 15 Hz, 6-H_2), and 3.80 (t, *J* 5.5 Hz, 2-H); δ_C 16.55 (C-2), 19.8 and 20.5 (4- and 5-Me), 22.4 (C-6), 35.8 (C-3), 120.55 (CN), and 126.8 and 127.0 (4- and 5-C). The cycloadduct (**9e**) was accompanied by a small amount of 2-*cyano*-2-*cyanomethylseleno*-3,6-*dihydro*-4,5-*dimethyl*-2H-*selenine* (**18e**), b.p. 230—235 °C (0.05 mmHg, Kugelrohr distillation) (Found: M^+, 319.9336. $C_{10}H_{12}N_2{}^{80}Se_2$ requires *M*, 319.9330); $\nu_{max.}$(liquid film) 2 240 and 2 220 cm^{-1}; δ_H 1.70 and 1.75 (2 × br s, 4- and 5-Me), 2.78 (m, 3-H_2), 3.10 (s, $SeCH_2CN$), and 3.28 (m, 6-H_2).

Cycloadducts (**12a**) *and* (**13a**) *of Cyclopentadiene and Ethyl Selenoxoacetate* (**1a**), *and the Corresponding Diseleno Derivatives* (**19a**): *Preparation from the Phthalimido Derivative* (**8a**).—The phthalimido derivative (**8a**), cyclopentadiene, and triethylamine (0.1 mol equiv.) gave, as described for the cycloadduct (**9a**), a mixture (*ca.* 1:1) of *ethyl* endo- (**12a**) and *ethyl* exo-2-*selenabicyclo*[2.2.1]*hept*-5-*ene*-3-*carboxylate* (**13a**) (64%), b.p. 130—135 °C (0.3 mmHg, Kugelrohr distillation) [Found: C, 46.5; H, 5.3%; M^+, 231.9989. $C_9H_{12}O_2Se$ requires C, 46.8; H, 5.2%; *M*(^{80}Se), 232.0002]; $\nu_{max.}$(liquid film) 1 730 cm^{-1}; δ(200 MHz; $CDCl_3$; standards: $CHCl_3$, δ_H 7.25; $CDCl_3$, δ_C 77.0) *endo*-isomer (**12a**), δ_H 1.22 (t, *J* 7.1 Hz, Me), 1.67 (dt, *J* 9.7 and *ca.* 1 Hz, 7-H), 1.79 (dt, *J* 9.7 and 2.4 Hz, 7-H), 3.47 (m, 4-H), 4.09 (q, *J* 7.1 Hz, OCH_2), 4.39 (m, 1-H), 4.71 (d, *J* 3.9 Hz, with ^{77}Se satellites, J_{HSe} 19 Hz, 3-H), 5.92 (dd, *J* 5.4 and 3.1 Hz, 5-H), and 6.50 (dd, *J* 5.4 and 3.0 Hz, 6-H); δ_C 14.1 (Me), 47.9 (C-4), 49.2 (CHSe, with ^{77}Se satellites, J_{CSe} 45.4 Hz), 50.83 (CHSe, with ^{77}Se satellites, J_{CSe} 69.7 Hz), 52.7 (C-7), 61.0 (OCH_2), 131.0 and 138.4 (C-5 and -6), and 172.5 (CO_2Et); *exo*-isomer (**13a**), δ_H 1.26 (t, *J* 7.1 Hz, Me), 1.86 (dt, *J* 10.1 and 2.2 Hz, 7-H), 2.06 (dt, *J* 10.1 and 0.6 Hz, 7-H), 3.30 (m, 4-H), 3.57 (s, with ^{77}Se satellites, J_{HSe} 12.1 Hz, 3-H), 4.19 (q, *J* 7.1 Hz, OCH_2), 4.45 (m, 1-H), 5.78 (dd, *J* 5.3 and 3.3 Hz, 5-H), and 6.42 (dd, *J* 5.3 and 2.8 Hz, 6-H); δ_C 14.1 (Me), 48.0, 48.1, and 48.7 (C-1, -3, and -4), 50.9 (C-7), 61.1 (OCH_2), 132.2 and 139.4 (C-5 and -6), and 174.5 (CO_2Et). The cycloadducts (**12a**) and (**13a**) were accompanied by a small amount of the stereoisomeric *diseleno derivatives* (**19a**) (characterised as a mixture) (Found: M^+ 397.9556. $C_{13}H_{18}O_4{}^{80}Se_2$ requires *M*, 397.9534); δ_H 1.28 (2 × t, *J* 7 Hz, 2 × Me), 3.75 (s, $SeCH_2CO_2Et$), 4.25 (2 × q, *J* 7 Hz, 2 × OCH_2), and 5.85, 6.0, 6.35, and 6.65 (4 × m, vinyl-H).

Preparation of (**12a**) *and* (**13a**) *from the Selenosulphonate* (**7a**).—The selenosulphonate (**7a**), cyclopentadiene, calcium chloride, and triethylamine gave, as described for the cycloadduct (**9a**), a mixture (*ca.* 1:1) of the cycloadducts (**12a**) and (**13a**) (63%).

Cycloadducts (**14a**) *and* (**15a**) *of Cyclohexa*-1,3-*diene and Ethyl Selenoxoacetate* (**1a**), *and the Corresponding Diseleno Derivatives* (**20a**), *Prepared from the Phthalimido Derivative* (**8a**).—The phthalimido derivative (**8a**), cyclohexa-1,3-diene, and triethylamine (0.1 mol equiv.) gave, as described for the cycloadduct (**9a**), a mixture (*endo*:*exo* ratio, 77:23) of *ethyl* endo- (**14a**) and *ethyl* exo-2-*selenabicyclo*[2.2.2]*oct*-5-*ene*-3-*carboxylate* (**15a**) (26%), b.p. 158—160 °C (0.1 mmHg, Kugelrohr distillation [Found: C, 49.2; H, 5.7%; M^+, 246.0147. $C_{10}H_{14}O_2Se$ requires C, 49.0; H, 5.8%; *M* (^{80}Se), 246.0159]; $\nu_{max.}$(liquid film) 1 730 cm^{-1}; δ(200 MHz; $CDCl_3$; standards: $CHCl_3$, δ_H 7.25, and $CDCl_3$, δ_C 77.0) *endo*-isomer (**14a**), δ_H 1.19 (t, *J* 7.1 Hz, Me), 1.35—2.4 (m, CH_2CH_2), 3.21 (m, 4-H), 3.69 (dtd, *J* 7.0, 3.0, and 1.1 Hz, 1-H), 4.06 (q, *J* 7.1 Hz, OCH_2), 4.31 (d, *J* 2.9 Hz, with ^{77}Se satellites, J_{HSe} 15.1 Hz, 3-H), 6.21 (td, *J* 7.5 and 1.0 Hz, 5-H), and 6.50 (td, *J* 7.5 and 1.0 Hz, 6-H); δ_C 14.0 (Me), 24.1 and 29.1 (CH_2), 29.9 and 30.9 (CH), 46.4 (C-3, with ^{77}Se satellites, J_{CSe} 67.8 Hz), 60.8 (OCH_2), 131.6 and 135.2 (C-5 and -6), and 172.5 (CO_2Et); *exo*-isomer (**15a**), δ_H 1.26 (t, *J* 7.1 Hz, Me), 1.75—2.40 (m, CH_2CH_2), 3.11 (m, 4-H), 3.69 (m, 1-H), 3.77 (t, *J* 1.9 Hz, with ^{77}Se satellites, J_{HSe} 8.9 Hz, 3-H), 4.19 (q, *J* 7.1 Hz, OCH_2), 6.23 (td, *J* 7.5 and 1.0 Hz, 5-H), and 6.49 (td, *J* 7.5 and 1.0 Hz, 6-H); δ_C 14.1 (Me), 19.7 and 29.6 (CH_2), 30.4 and 31.1 (CH), 44.8 (C-3), 61.0 (OCH_2), 132.5 and 135.5 (C-5 and -6), and 171.6 (CO_2Et). The cycloadducts (**14a**) and (**15a**) were accompanied by a small amount of the stereoisomeric diseleno derivatives (**20a**), obtained as a mixture; δ_H 1.26 (2 × t, *J* 7 Hz, 2 × Me), 1.5—2.7 (m, CH_2CH_2), 3.32 (s, $SeCH_2CO_2Et$), 3.33 (m, 4-H), 3.75 (m, 1-H), 4.18 (2 × q, *J* 7 Hz, 2 × OCH_2), and 6.2—6.7 (m, vinyl-H).

Cycloadduct (**16a**) *of Anthracene and Ethyl Selenoxoacetate* (**1a**) *and the Corresponding Acid* (**16**; Z = CO_2H): *Preparation from the Selenenyl Chloride* (**6a**).—The selenenyl chloride (**6a**), prepared as described before from the diselenide (**5a**) (5.0 g, 15 mmol) and sulphuryl chloride (2.03 g, 15 mmol) in benzene (40 ml), was added slowly in chloroform (200 ml) during 15 min to anthracene (26.7 g, 150 mmol) and triethylamine (3.03 g, 30 mmol) in chloroform (500 ml) with heating under reflux. After a further 15 min the mixture was cooled to 0 °C and set aside to allow anthracene to crystallise out. The mixture was filtered and the filtrate was washed with dilute hydrochloric acid then with water and was dried and evaporated. Chromatography gave *ethyl* 9,10-*dihydro*-10,9-(*episelenomethano*)*anthracene*-12-*carboxylate* (**16a**) (2.88 g, 28%), m.p. 147—149 °C (from diethyl ether) (Found: C, 62.7; H, 4.7. $C_{18}H_{16}O_2Se$ requires C, 63.0; H, 4.7%); $\nu_{max.}$ 1 720 cm^{-1}; δ_H 1.15 (t, *J* 7 Hz, Me), 4.08 (q, *J* 7 Hz, OCH_2), 4.35 (d, *J* 3 Hz, 12-H), 4.93 (d, *J* 3 Hz, 9-H), 5.32 (s, 10-H), and 7.05—7.55 (m, ArH); δ_C 14.0 (Me), 39.5, 47.0, and 50.6 (C-9, -10 and -12), 61.4 (OCH_2), 121.3, 122.2, 124.85, 125.8, 126.2, 126.7, 126.9, and 128.0 (ArCH), 139.2, 141.9, 142.9, and 143.8 (ArC), and 171.5 (CO_2Et). Hydrolysis of the ethyl ester in aqueous ethanolic sodium hydroxide at room temperature gave 9,10-*dihydro*-10,9-(*episelenomethano*)*anthracene*-12-*carboxylic acid* (**16**; Z = CO_2H), m.p. 183—184 °C (from benzene–diethyl ether), as a benzene solvate (Found: C, 66.9; H, 4.7. $C_{16}H_{12}O_2Se{\cdot}C_6H_6$ requires C, 67.2; H, 4.6%); $\nu_{max.}$ 1 700 cm^{-1}; δ_H 4.32 (d, *J* 3 Hz, 12-H), 4.83 (d, *J* 3 Hz, 9-H), 5.28 (s, 10-H), 6.9—7.4 (14 H, ArH), and 7.7 (br s, exch. with D_2O, CO_2H); δ_C 39.75, 46.8, and 50.7 (C-9, -10, and -12), 121.3, 122.2, 124.9, 126.0, 126.3, 126.8, 127.0, 127.9 (ArCH), 138.7, 141.5, 142.7, and 143.6 (ArC), and 177.6 (CO_2Et).

Preparation of (**16a**) *from the Phthalimido Derivative* (**8a**).—The phthalimido derivative (**8a**), anthracene, and triethylamine (0.1 mol equiv.) gave, as described for the cycloadduct (**9a**), the cycloadduct (**16a**) (32%).

Cycloadduct (**17a**) *of* 9,10-*Dimethylanthracene and Ethyl Selenoxoacetate* (**1a**), *Prepared from the Phthalimido Derivative* (**8a**).—The selenenyl chloride (**6a**) (1.00 mmol), prepared as described before from the diselenide (**5a**) and sulphuryl chloride, was added dropwise during 15 min in chloroform (50 ml) to equimolecular amounts of 9,10-dimethylanthracene [18] and triethylamine in chloroform (40 ml) with heating under reflux. The mixture was heated further for 15 min and was then cooled and washed with dilute hydrochloric acid and then water. The chloroform solution was dried and evaporated. Chromatography of the residue gave *ethyl* 9,10-*dihydro*-9,10-*dimethyl*-10,9-(*episelenomethano*)*anthracene*-12-*carboxylate* (**17a**) (61%), m.p. 84—86 °C (from light petroleum) (Found: C, 64.9; H, 5.5. $C_{20}H_{20}O_2Se$ requires C, 64.7; H, 5.4%); $\nu_{max.}$(thin film) 1 740 cm^{-1}; δ_H 1.08 (t, *J* 7 Hz, OCH_2Me), 3.23 and 3.34 (2 × s, 9- and 10-Me), 4.02 (q, *J* 7 Hz, OCH_2), 4.12 (s, 12-H), and 7.1—7.55 (m, ArH); δ_C 14.0 (OCH_2Me), 17.8 and 18.3 (9- and 10-Me), 43.15 and 45.0 (C-9 and -10), 55.3 (C-12), 60.9 (OCH_2), 118.4, 122.1, 125.2, 125.4, 125.8, 126.2, and 126.5 (ArCH), and 141.7, 144.3 145.2, and 146.05 (ArC), and 171.7 (CO_2Et).

Cycloadduct (**17c**) *of* 9,10-*Dimethylanthracene and* 2-*Oxo*-3-*phenylethaneselenal* (**1c**), *Prepared from the Selenocyanate* (**3c**).—Equimolecular amounts of the selenocyanate (**3c**), 9,10-dimethylanthracene, triethylamine, and calcium chloride dihydrate gave, as described for the cycloadduct (**9a**) (but note that an excess of the 'diene' was not used here), 12-*benzoyl*-9,10-*dihydro*-9,10-*dimethyl*-10,9-(*episelenomethano*)*anthracene* (**17c**) (13%), m.p. 187—188 °C (from propan-2-ol) (Found: C, 71.1; H, 5.0. $C_{24}H_{20}OSe$ requires C, 71.4; H, 5.0%); $\nu_{max.}$ 1 685 cm^{-1}; δ_H 2.32 and 2.37 (2 × s, 9- and 10-Me), 5.05 (s, 12-H), and 7.2—7.8 (m, ArH); δ_C 17.7 and 18.4 (9- and 10-Me), 44.7 and 45.25 (C-9 and -10), 58.0 (C-12), 118.4, 118.6, 122.4, 125.6, 125.9, 126.5, 127.4, 127.8, 128.6, 133.2, 138.1, 142.5, 144.9, 145.3, 146.3, and 146.8 (ArC), and 195.2 (Ph*C*O).

Cycloadduct (**17e**) *of* 9,10-*Dimethylanthracene and Selenoxoacetonitrile* (**1e**), *Prepared from the Selenosulphate* (**4e**).—Equimolecular amounts of the selenosulphate (**4e**), 9,10-dimethylanthracene, triethylamine, and calcium chloride dihydrate gave, as described for the cycloadduct (**9a**) (but note that an excess of the 'diene' was not used here), 12-*cyano*-9,10-*dihydro*-9,10-*dimethyl*-10,9-(*episelenomethano*)*anthracene* (**17e**) (25%), m.p. 156—158 °C (from diethyl ether) (Found: C, 66.9; H, 4.5; N, 4.3. $C_{18}H_{15}NSe$ requires C, 66.7; H, 4.7; N, 4.3%); $\nu_{max.}$ 2 230 cm^{-1}; δ_H 2.30 (s, 9- and 10-Me), 3.95 (s, with ^{77}Se satellites, J_{HSe} 14 Hz, 12-H), and 7.1—7.6 (m, ArH); δ_C 18.1 and 18.6 (9- and 10-Me), 40.2 (C-12), 44.4 and 45.5 (C-9 and -10), 118.7, 119.1, 122.8. 124.0, 126.3, 126.5, and 127.4 (ArC), and 126.2 (CN).

Cycloadducts (**28**) *and* (**29**) *of Thebaine* (**27**) *and Ethyl Selenoxoacetate* (**1a**): *Preparation from the Selenosulphonate* (**7a**).—Equimolecular amounts of the selenosulphonate (**7a**), thebaine (**27**), triethylamine, and calcium chloride dihydrate gave, as described for the cycloadduct (**9a**) (but note that an excess of the 'diene' was not used here), the 7α-(**28**) and 7β-isomers (**29**), which were separated chromatographically. *Ethyl* 6,7,8,14-*tetrahydro*-6α,14α-*etheno*-8-*selenathebaine*-7α-*carboxylate* (**28**) (22%) had m.p. 129—131 °C (from propan-2-ol) (Found: C, 58.1; H, 6.0; N, 2.8. $C_{23}H_{27}NO_5Se$ requires C, 58.0; H, 5.7; N, 2.9%); $\nu_{max.}$ 1 735 cm^{-1}; δ_H(200 MHz; $CDCl_3$; standard: $CHCl_3$, δ 7.25) 1.21 (t, *J* 7.1 Hz, OCH_2Me), 2.36 (s, NMe), 2.51 (dd, *J* 18.5 and 6.5 Hz, 10α-H), 3.19 (d, *J* 18.5 Hz, 10β-H), 3.42 (d, *J* 6.5 Hz, 9-H), 3.63 (s, 6-OMe), 3.81 (s, 3-OMe), 4.11 (q, *J* 7.1 Hz, OCH_2Me), 4.26 (d, *J* 0.7 Hz, with ^{77}Se satellites, J_{HSe} 16.8 Hz, 7-H), 4.49 (d, *J* 1.5 Hz, 5-H), 5.83 (d, *J* 9.1 Hz, 19-H), 5.92 (ddd, *J* 9.2, 1.5, and 0.7 Hz, 18-H), 6.54 (d, *J* 8.2 Hz, 1-H), and 6.63 (d, *J* 8.2 Hz, 2-H); δ_C(50.4 MHz; $CDCl_3$; standard $CDCl_3$, δ 77.0) 14.0 (OCH_2Me), 23.0 (C-10), 34.6 (C-15), 43.5 (NMe), 44.15 (C-7), 45.9 (C-16), 51.1 (C-13), 51.85 (C-14), 52.9 (6-OMe), 56.6 (3-OMe), 60.75 (C-9), 61.0 (OCH_2Me), 80.2 (C-6), 92.4 (C-5), 113.8 (C-2), 119.7 (C-1), 126.5 (C-11), 127.5 (C-19), 133.7 (C-12), 133.9 (C-18), 142.1 (C-3), 146.8 (C-4), and 170.5 (CO_2Et). *Ethyl* 6,7,8,14-*tetrahydro*-6α,14α-*etheno*-8-*selenathebaine*-7β-*carboxylate* (**29**) (19%) had m.p. 150—153 °C (from propan-2-ol) (Found: C, 57.9; H, 5.7; N, 2.7%); $\nu_{max.}$ 1 730 cm^{-1}; δ_H[200 MHz; as for (**28**)] 1.29 (t, *J* 7.1 Hz, OCH_2Me), 2.37 (s, NMe), 2.49 (dd, *J* 18.6 and 6.6 Hz, 10α-H), 3.21 (d, *J* 18.6 Hz, 10β-H), 3.37 (d, *J* 6.6 Hz, 9H), 3.59 (s, 6-OMe), 3.81 (s, 3-OMe), 3.88 (s, with ^{77}Se satellites, J_{HSe} 9.6 Hz, 7-H), 4.21 (q, *J* 7.1 Hz, OCH_2Me), 5.73 (d, *J* 0.8 Hz, 5-H), 5.84 (m, 18- and 19-H), 6.51 (d, *J* 8.1 Hz, 1-H), and 6.63 (d, *J* 8.1 Hz, 2-H); δ_C[50.4 MHz; as for (**28**)] 14.1 (OCH_2Me), 23.0 (C-10), 32.7 (C-15), 43.5 (NMe), 45.05 (C-7), 45.9 (C-16), 50.0 (C-13), 52.4 (C-14), 53.5 (6-OMe), 56.8 (3-OMe), 61.0 (C-9), 61.4 (OCH_2Me), 80.4 (C-6), 90.3 (C-5), 114.2 (C-2), 119.2 (C-1), 125.7 (C-19), 126.5 (C-11), 134.25 (C-12), 136.75 (C-18), 142.2 (C-3), 147.3 (C-4), and 171.7 (CO_2Et).

Preparation of the Cycloadducts (**28**) *and* (**29**) *from the Phthalimido Derivative* (**8a**).—Equimolecular amounts of the phthalimido derivative (**8a**), thebaine (**27**), and triethylamine gave, as described for the cycloadduct (**9a**) (but note that an excess of the 'diene' was not used here), a mixture (35%) of the 7α- (**28**) and 7β-isomers (**29**) (α:β ratio, 55:45).

Reaction of 2,3-*Dimethylbuta*-1,3-*diene with* Se-*Ethoxycarbonylmethyl Toluene*-4-*selenosulphonate* (**7a**): *Formation of the* 1,2-*Adduct* (**10**; X = EtO) *in Ethanol*.—Triethylamine (0.99 mmol) in ethanol (5 ml) was added slowly during 15 min to the selenosulphonate (**7a**) (0.78 mmol), 2,3-dimethylbuta-1,3-diene (3.9 mmol), and calcium chloride dihydrate (0.78 mmol) in ethanol (25 ml) with heating under reflux. Heating was continued for a further 15 min and then the mixture was worked up, as described for the preparation of the cycloadduct (**9a**), to give the cycloadduct (**9a**) (18%) and *ethyl* 5-*ethoxy*-5,6-*dimethyl*-3-*selenahept*-6-*enoate* (**10**; X = EtO) (31%), b.p. 100—105 °C (0.06 mmHg, Kugelrohr distillation) (Found: C, 48.9; H, 7.7. $C_{12}H_{22}O_3Se$ requires C, 49.1; H, 7.5%); $\nu_{max.}$(liquid film) 1 735 cm^{-1}; δ_H 1.3 and 1.28 (2 × t, *J* 7 Hz, 2 × OCH_2Me), 1.42 and 1.74 (2 × s, 2 × Me), 2.95 and 3.15 [AB system, *J* 12 Hz, 4-H_2], 3.20 (s, $SeCH_2CO_2Et$), *ca.* 3.2 [m, 5-OCH_2Me], 4.18 (q, *J* 7 Hz, CO_2CH_2Me), and 4.98 (br s, 7-H_2).

Formation of the 1,4-*Adducts* (**11**; X = 4-$MeC_6H_4SO_2$) *in Benzene*.—The selenosulphonate (**7a**) (0.78 mmol) in benzene (5 ml) was added dropwise during 15 min to 2,3-dimethylbuta-1,3-diene (3.9 mmol) in benzene (25 ml) with heating under reflux. Heating was continued for 15 min then the mixture was worked up in the usual way to give *ethyl* 5,6-*dimethyl*-7-(4-*tolylsulphonyl*)-3-*selenahept*-5-*enoate* (**11**; X = 4-$MeC_6H_4SO_2$) as a mixture (*ca.* 1:1) of geometrical isomers; $\nu_{max.}$(liquid film) 1 730 cm^{-1}. The E-*isomer* had m.p. 69—71 °C (from light petroleum–diethyl ether) (Found: C, 50.6; H, 5.7. $C_{17}H_{24}O_4SSe$ requires C, 50.6; H, 6.0%); δ_H 1.28 (t, *J* 7 Hz, OCH_2Me), 1.46 and 1.85 (2 × s, 5- and 6-Me), 2.45 (s, ArMe), 3.11 and 3.45 (2 × s, 2- and 4-H_2), 3.86 (s, CH_2SO_2), 4.25 (q, *J* 7 Hz, OCH_2), and 7.30 and 7.75 (AB system, *J* 8 Hz, ArH). The oily *Z*-isomer gave δ_H 1.28 (t, *J* 7 Hz, OCH_2Me), 1.81 (br s, 5- and 6-Me), 2.45 (s, ArMe), 2.97 and 3.21 (2 × s, 2- and 4-CH_2), 3.98 (s, CH_2SO_2), 4.25 (q, *J* 7 Hz, OCH_2), and 7.30 and 7.75 (AB system, *J* 8 Hz, ArH).

Reaction of 2,3-*Dimethylbuta*-1,3-*diene with Ethoxycarbonylmethaneselenenyl Chloride* (**6a**) *to Form the* 1,2- (**10**; X = Cl) *and* 1,4-*Adduct* (**11**; X = Cl).—The selenenyl chloride (**6a**) was added slowly in benzene to 2,3-dimethylbuta-1,3-diene (5 mol equiv.), also in benzene, either at room temperature or with heating under reflux. Complex mixtures resulted at both temperatures, the lower temperature favouring formation of the 1,2-adduct and the high favouring the 1,4-adduct. Both products were oils that decomposed partially upon distillation. Ethyl 5-chloro-5,6-dimethyl-3-selenahept-6-enoate (**10**; X = Cl) gave δ_H 1.28 (t, *J* 7 Hz, OCH_2Me), 1.41 (s, 5-Me), 1.78 (s, 6-Me), 1.90 (d, *J* 13 Hz, 4-CH_AH_B), 3.30 (s, 2-H_2), 3.30 (d, *J* 13 Hz, 4-CH_AH_B), 4.22 (q, *J* 7 Hz, OCH_2Me), and 4.90 and 5.10 (2 × m, 7-H_2); δ_C 14.1 (OCH_2Me), 19.3 (6-Me), 23.6 and 38.7 (C-2 and -4), 27.0 (5-Me), 61.4 (OCH_2Me), 74.4 (C-5), 110.8 (C-7), 149.3 (C-6), and 171.9 (CO_2Et). Ethyl 7-chloro-5,6-dimethyl-3-selenahept-5-enoate (**11**; X = Cl) gave δ_H 1.26 (t, *J* 7 Hz, OCH_2Me), 1.85 (m, 5- and 6-Me), 3.10 (s, with ^{77}Se satellites, J_{HSe} 15 Hz, 2-H_2), 3.55 (m, 4-H_2), 4.10 (m, 7-H_2), and 4.20 (q, *J* 7 Hz, OCH_2Me).

Retro-Diels–Alder Reactions of the Cyclopentadiene Cycloadducts (**12a**) *and* (**13a**).—The *endo*- (**12a**) and *exo*-isomer (**13a**) were heated in turn in toluene under reflux for 10 and 7 h, respectively, to give mixtures having the same composition; *endo*-(**12a**):*exo*-(**13a**) ratio, 3:7. A mixture of the cycloadducts (**12a**) and (**13a**) (ratio, 7:3) (0.43 mmol), prepared as before, and 2,3-dimethylbuta-1,3-diene (0.5 mmol) was heated in toluene (10 ml) in a sealed tube at 100 °C for 21 h to give, after distillation of the crude product, the cycloadduct (**9a**) (85%).

Retro-Diels–Alder Reactions of the Anthracene Cycloadducts (**16**).—The cycloadducts (**16a**) (100 mg) and 2,3-dimethylbuta-1,3-diene (1 mol equiv.) were heated in toluene (10 ml) in a sealed tube at 120 °C for 5 h to afford, after chromatography of the crude product, the cycloadduct (**9a**) (87%). Equimolecular amounts (0.29 mmol) of the cycloadduct (**16a**), the corresponding sulphur compound (**16a**; Se = S), and 2,3-dimethylbuta-1,3-diene were heated in benzene (20 ml) in a sealed tube at 100 °C for 5 h. Chromatography of the reaction mixture gave the selenine (**9a**) and the thiine (**9a**; Se = S) (combined yield, 64%) in the ratio 42:58 (by ^{1}H n.m.r. spectroscopy at 200 MHz).

Retro-Diels–Alder Reactions of the 9,10-*Dimethylanthracene Cycloadducts* (**17**).—The cycloadducts (**17c**) and (**17e**) (0.29 mmol) of 9,10-dimethylanthracene were heated in turn with 2,3-dimethylbuta-1,3-diene (0.29 mmol) in benzene (15 ml) in a sealed tube at 110—120 °C for 5 h to give, after chromatography of the crude product, the corresponding cycloadducts of dimethylbutadiene (**9c**) (91%) and (**9e**) (88%). Similarly, the cycloadduct (**17a**) (0.29 mmol) and 2,3-dimethylbuta-1,3-diene (0.29 mmol) were heated under reflux in benzene (15 ml) for 1 h to afford the cycloadduct (**9a**) (*ca.* 40%, ^{1}H n.m.r. control). In contrast, the anthracene adduct (**16a**) gave, under the same conditions, only *ca.* 5% of the cycloadduct (**9a**).

Note added in proof. A recent paper (P. T. Meinke and G. A. Krafft, *Tetrahedron Lett.*, 1987, 5121) reports that the electrophilic selenoaldehydes (**1a**), (**1c**), (**1e**), and MeCOCHSe, prepared by our method[16] from the corresponding selenocyanates (**3**), react regioselectively with penta-1,3-diene and 2-methylpenta-1,3-diene to give mixtures of cycloadducts having *endo*:*exo* ratios of *ca.* 1:1. This contrasts with the high *endo* selectivity observed.[12] in cycloadditions of selenoxoalkanes (RCHSe) with cyclopentadiene, and supports our conclusions on reactivity and stereoselectivity. Unfortunately, the stereoselectivity of cycloadditions of RCHSe with the pentadienes could not be determined, since trapping with these less reactive dienes was unsuccessful.

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