A New Method for Radical Generation: Reductive C–Se or C–S Bond Cleavage of Cyclic Onium Salts

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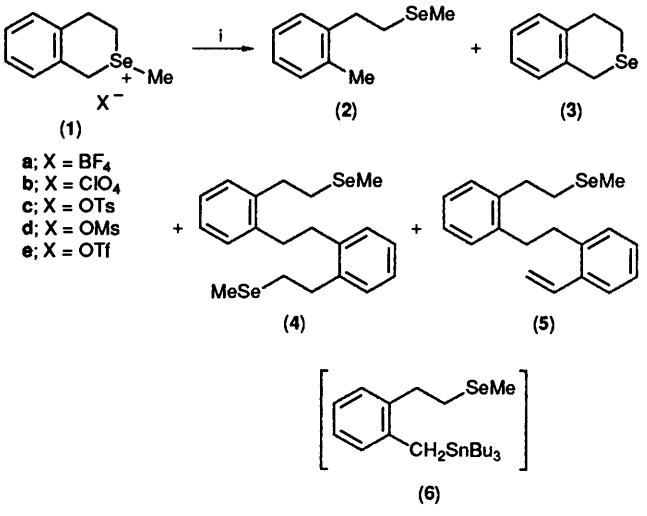
2-Methyl-3,4-dihydro-1*H*-2-benzoselenopyranium salt (**1**) was reduced by some metallic reagents or magnesium metal *via* the single-electron transfer (SET) process to give 2-[2-(methylseleno)ethyl]-toluene (**2**). Magnesium metal was a good SET reducing agent. Some other selenonium or sulphonium salts (**7**), (**14**), (**22**), (**27**) and (**32**) were similarly reduced by magnesium. Particularly, sonication accelerated the reductions. ε-Eneselenonium salt (**43**) was treated with activated magnesium to give a cyclised pyrrolidine derivative (**44**).

Triarylsulphonium salts and diaryl sulphoxides react with organometallic reagents to give the corresponding sulphuranes, which decompose to some ligand-coupled products or to exchange their substituents on the sulphur atom.[1] Oae's group has been extensively studying sulphuranes and ligand-coupling reactions.[2] Selenonium salts also react with organolithium compounds to form selenuranes[3] or undergo ligand exchange on the selenium atom.[4]

Recently, we have reported that cyclic selenonium salts underwent SET reduction by Grignard reagents or magnesium metal.[5] This novel reaction can be used for the easy cleavage of the C–Se bond of other selenonium salts. We report here a comparison of this reaction with other SET reductions and its applications to some cyclic sulphonium salts.

Results and Discussion

Reduction of 2-*Methyl*-3,4-*dihydro*-1H-2-*benzoseleno*(*or thio*)*pyranium Salts* (**1**) *and* (**7**).—2-Methyl-3,4-dihydro-1*H*-2-benzoselenopyranium tetrafluoroborate (**1a**) reacted with methylmagnesium iodide (3 mol equiv.) to give 2-[2-(methylseleno)ethyl]toluene (**2**) in 68% yield (Scheme 1 and Table 1, Entry 1). The structure of product (**2**) was determined by comparison with an authentic sample prepared by an alternative method.[5] The reactions of compound (**1a**) with other Grignard reagents, ethyl- and phenyl-magnesium iodides, similarly afforded compound (**2**) in 73% and quantitative yield, respectively (Entries 2 and 4). When this reaction was achieved in refluxing tetrahydrofuran (THF), demethylated product (**3**) was the main product (Entry 3). Under these conditions, the Grignard reagent would nucleophilically attack the methyl group. By contrast, reactions of compound (**1a**) with alkylmagnesium bromides did not proceed. Exceptionally, the reaction with allylmagnesium bromide, a fairly good SET reagent,[6] provided compound (**2**) in 50% yield (Entry 5).



Scheme 1. *Reagent:* i, metallic reagent.

Next, we investigated the effects of counter-anions of some selenonium salts (**1a–e**) on their reactivity with ethylmagnesium iodide (Entries 2 and 6–9). Tetrafluoroborate (**1a**) and perchlorate (**1b**) similarly produced compound (**2**) in good yield. Although the reaction of tosylester (**1c**) afforded compound (**2**) in 52% yield; mesyl (**1d**) and triflate (**1e**) esters afforded compound (**2**) in low yield. These findings are in contrast to those that the counter-anions did not influence the reactivity of selenonium salts with some nucleophiles.[7] From these results, the lower the nucleophilicity of the counter-anion, the more easily does the selenonium salt accept a single electron from the Grignard reagent. Consequently, tetrafluoroborate and perchlorate, which have no nucleophilicity, are suitable for radical generation.

Reaction of compound (**1a**) with butyl-lithium (1.1 mol equiv.) afforded compound (**2**) (7%), a dimeric product (**4**) (13%) and the ene selenide (**5**)† (16%) (Entry 10). The difference between the reaction with the Grignard reagents and that with butyl-lithium may be ascribed to the difference in their ionic nature; butyl-lithium is more ionic than Grignard reagents.[8]

In order to examine the SET reduction of the selenonium salts with metals some more experiments were conducted. Magnesium metal reduced the selenonium salt (**1a**) to give selenide (**2**) (Entries 11–15). It took a long time (> 12 h) for completion of the reaction because the surface of magnesium metal was deactivated by the magnesium tetrafluoroborate formed during the reaction, and the salt (**1a**) was not sufficiently soluble in solvents. However, this reaction gradually proceeded without formation of any by-product (Entries 12 and 13). THF was a more suitable solvent than either diethyl ether or benzene. Selenonium salt (**1a**) was dissolved in

† Compound (**5**) would be produced as follows: 2-(methylselenomethyl)styrene formed by β-elimination of compound (**1a**) is deselenated by butyl-lithium to produce 2-vinylbenzyl-lithium. The benzyl-lithium reacts nucleophilically with a second molecule of salt (**1a**) to give the ring-opened product (**5**).

Table 1. Reaction of 2-methyl-3,4-dihydro-1*H*-2-benzoselenopyranium salts (**1**) with metallic reagents.

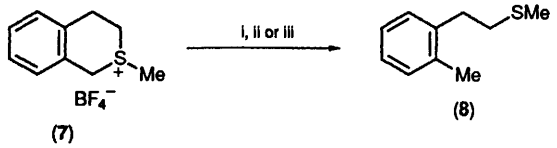
Entry	Substrate	Reagent	Solvent	Conditions	Products (% yield)
1	(**1a**)	MeMgI	THF	0 °C, 5 h	(**2**) (68), (**3**) (trace)
2	(**1a**)	EtMgI	THF	0 °C, 5 h	(**2**), (73), (**3**) (2)
3	(**1a**)	EtMgI	THF	reflux, 1 h	(**2**) (trace), (**3**) (89)
4	(**1a**)	PhMgI	THF	room temp., 18 h	(**2**) (quant.)
5	(**1a**)	CH_2CHCH_2MgBr	THF	room temp., 30 h	(**2**) (50)
6	(**1b**)	EtMgI	THF	0 °C, 5 h	(**2**) (70), (**3**) (trace)
7	(**1c**)	EtMgI	THF	0 °C, 5 h	(**2**) (52), (**3**) (5)
8	(**1d**)	EtMgI	THF	0 °C, 5 h	(**2**) (21), (**3**) (3)
9	(**1e**)	EtMgI	THF	0 °C, 5 h	(**2**) (9), (**3**) (3)
10	(**1a**)	BuLi	THF	−78 °C to room temp., 12 h	(**2**) (7), (**4**) (13), (**5**) (16)
11	(**1a**)	Mg	THF	room temp., 12 h	(**2**) (82)
12	(**1a**)	Mg	Et_2O	room temp., 30 h	(**2**) (71)
13	(**1a**)	Mg	C_6H_6	room temp., 30 h	(**2**) (62)
14	(**1a**)	Mg	DMF	room temp., 30 h	(**2**) (52)
15	(**1a**)	Mg	THF	sonication room temp., 15 min	(**2**) (86)
16	(**1a**)	Zn	AcOH	room temp., 12 h	(**2**) (94)
17	(**1a**)	Zn	THF	room temp., 30 h	(**2**) (trace)
18	(**1a**)	Bu_3SnH[a]	C_6H_6	reflux, 1 h	(**2**) (52)
19	(**1a**)	$LiAlH_4$	THF	room temp., 18 h	(**2**) (20), (**3**) (50), (**4**) (24)
20	(**1a**)	$NaBH_4$	EtOH	reflux, 30 min	(**2**) (50), (**3**) (12)

[a] In the presence of catalytic amounts of AIBN.

N,*N*-dimethylformamide (DMF), but the reaction proceeded very slowly. On the other hand, when the surface of the magnesium was activated by sonication, the reaction was extremely fast and afforded the selenide (**2**) in excellent yield even after 15 min. Extension of reaction time decreased the yield of selenide (**2**). The reaction in the presence of iodine as a radical scavenger furnished compound (**2**) in 43% yield. Reduction of the salt (**1a**) with zinc–acetic acid similarly gave compound (**2**) in excellent yield (Entry 16),[9,10] but zinc or sodium in THF did not smoothly reduce the selenonium salt (**1a**).

Next, selenonium salt (**1a**) was reduced by metal hydride reagents (Entries 18–20). Reaction with tributyltin hydride afforded the benzyltin compound (**6**), which was unstable and decomposed to the selenide (**2**) during chromatography on silica gel (Entry 18). This reaction required catalytic amounts of azoisobutyronitrile (AIBN) even under reflux conditions. Reduction of compound (**1a**) with lithium aluminium hydride (LAH) afforded the selenide (**2**), demethylated product (**3**), and dimerised product (**4**) in 50, 20 and 24% yield, respectively (Entry 19). The intermolecular radical coupling reaction of the benzyl radical intermediate would be faster than hydrogen abstraction from the solvent. LAH is a single-electron reducing agent of alkyl halides. Hex-1-enyl iodide was reduced by LAH and formed a cyclopentane derivative through an SET process, but hex-1-enyl bromide, chloride and tosylester did not form cyclised products.[11] Reaction of compound (**1a**) with sodium borohydride was very slow at room temperature and the ethanolic solution was heated (Entry 20). Metal hydride reductions of salts (**1**) showed lower selectivities of the C–Se bond cleavage than did the reductions with Grignard reagents or magnesium.

A sulphur analogue (**7**) was similarly reduced by magnesium to give a sulphide (**8**) in 70% yield. The yield of compound (**8**) was lower than that of selenide (**2**) even by the use of sonochemically activated magnesium as shown in Scheme 2.



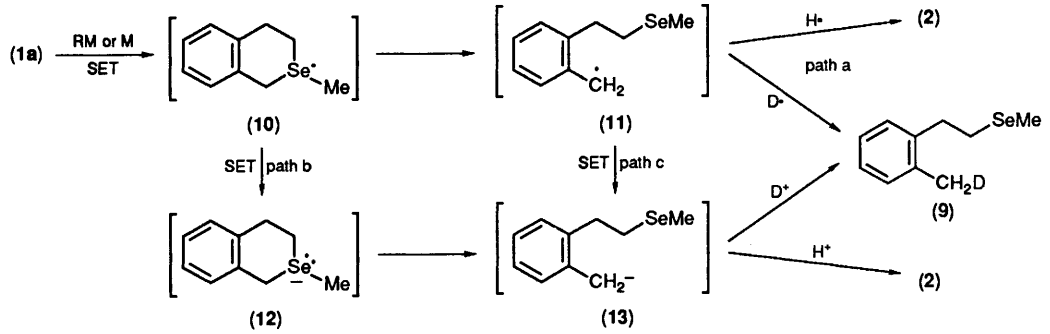
(**7**) (**8**)

Scheme 2. *Reagents and conditions:* (i) Mg, THF, room temp. 12 h (70%); (ii) Mg, sonication THF, room temp. 30 min (80%); (iii) Zn–AcOH, room temp. 12 h (16%).

Mechanistic Studies.—We propose a mechanism for the formation of 2-[2-(methylseleno)ethyl]toluene (**2**) in which the reaction is initiated by SET from the reducing agent to the selenonium salt (**1a**), as shown in Scheme 3, on the basis of the following results: (1) the product (**2**) was obtained from every reaction of the salt (**1a**) with methyl-, ethyl- or phenyl-magnesium iodide; (2) a striking difference was observed between the reactions with RMgI and with RMgBr; (3) the dimeric product (**4**) was produced from reaction with butyllithium.

The first intermediate, selenuranyl radical (**10**), is formed by SET reduction and then ring opens to afford a benzyl radical (**11**). The benzyl radical (**11**) abstracts a hydrogen atom from the solvent to form the toluene derivative (**2**) (path a in Scheme 3). The product (**4**) would be formed by dimerisation of the intermediate (**11**). On the other hand, formation of the toluene derivative (**2**) may also be explained in terms of an ionic process.

The selenuranyl radical (**10**) is further reduced to a selenuranyl anion (**12**), which decomposes to a benzyl anion (**13**). The benzyl anion (**13**) is also generated by SET reduction of the benzyl radical (**11**). Protonation of the anion (**13**) yielded the toluene derivative (**2**). In order to determine whether the reaction proceeds *via* the radical (**11**) or the anion (**13**), we conducted two experiments, reaction of (**1a**) with magnesium in [$^2H_8$]THF under ultrasonic irradiation and reaction of salt (**1a**) with zinc in CH_3CO_2D. Reduction with magnesium under sonication afforded the [α-^{2}H]toluene derivative (**9**). If the benzyl anion (**13**) were formed by the reduction with magnesium in [$^2H_8$]THF, the anion (**13**) should have reacted with the selenonium salt (**1a**) remaining in the reaction mixture much more easily than with THF. However, any product other than selenide (**2**) was not obtained as shown in Table 1. This finding indicates that reduction with magnesium proceeds through the radical (**11**). On the other hand, reduction with zinc in CH_3CO_2D also afforded the deuteriated product (**9**). In this method, the radical (**11**) abstracts a hydrogen from the methyl group and the anion (**13**) picks up a deuterium from the carboxy group. The experimental results indicate that reduction with



Scheme 3.

Table 2. Reductions of cyclic onium salts.

Entry	Substrate	Method[a]	Time (h)	Products (% yield)
1	(**14a**)	A	30	(**15a**) (44), (**16a**) (26)
2		B	0.5	(**15a**) (54), (**16a**) (26)
3		D	12	(**16a**) (54), (**17a**) (43)
4	(**14**)	A	30	(**15b**) (25), (**16b**) (15)
5		B	1	(**15b**) (42), (**16b**) (26)
6		D	12	(**16b**) (35), (**17b**) (25)
7	(**22a**)	A	30	(**23a**) (65)
8		B	0.5	(**23a**) (74)
9		D	12	(**23a**) (53), (**25**) (42)
10	(**22b**)	A	30	(**23b**) (74), (**24**) (trace)
11		B	1	(**23b**) (69), (**24**) (4)
12		D	12	(**23b**) (38), (**26**) (58)
13	(**27a**)	A	30	(**28a**) (50)
14		B	0.5	(**28a**) (63)
15		C	12	(**28a**) (68)
16		D	12	(**31a**) (21)
17	(**27b**)	A	30	(**28b**) (21)
18		B	1	(**28b**) (70)
19		C	12	(**28b**) (38)
20		D	12	(**31b**) (31)
21	(**32a**)	A	30	(**33a**) (86)
22		B	0.5	(**33a**) (50)
23		C	12	(**33a**) (40)
24		D	12	(**33a**) (82), (**36**) (16)
25	(**32b**)	A	30	(**33b**) (21), (**34**) (30), (**35**) (6)
26		B	1	(**33b**) (41), (**34**) (23), (**35**) (20)
27		C	12	(**33b**) (41), (**34**) (35), (**35**) (11)
28		D	12	(**37**) (60), (**38**) (6)

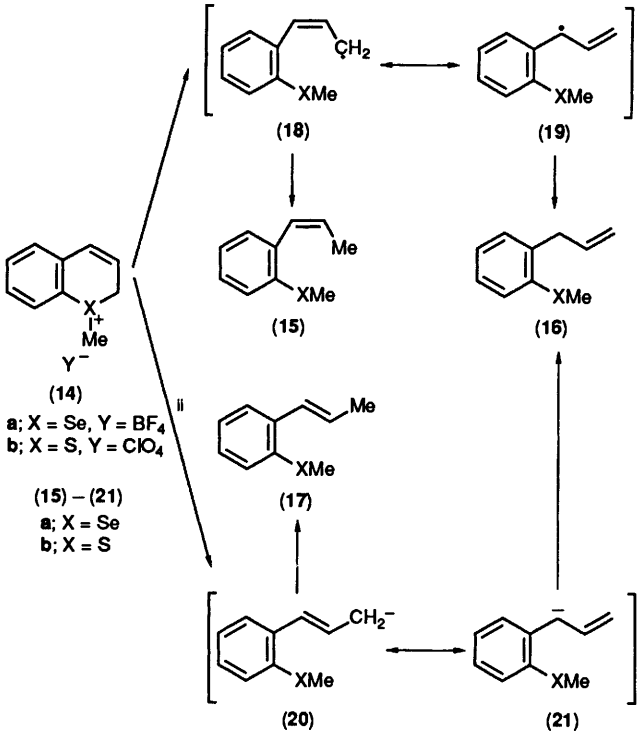
[a] Method A: magnesium (3 mol equiv.) in THF (0.05M-suspension) at room temperature. Method B: magnesium (3 mol equiv.) with sonication in THF (0.05M-suspension) at room temperature. Method C: magnesium–anthracene–THF complex (3 mol equiv.) in THF (0.05M) at room temperature. Method D: excess of zinc in acetic acid (0.05M-solution) at room temperature.

zinc–acetic acid goes through the anion (**13**). This mechanism is supported by the evidence that the dimeric product (**4**) was not formed in this reaction.

Both the selenonium salt (**1a**) and its sulphur analogue (**7**) underwent similar reductions, but the yield of the selenide (**2**) was higher than that of the analogous sulphide (**8**). We next measured the reduction potentials of the salts (**1a**) and (**7**) by cyclic voltammetry in acetonitrile using a hanging mercury drop electrode. Their voltammograms showed irreversible waves at a scan rate (v) of <200 V s^{-1}. The cathodic peak potentials of salts (**1a**) and (**7**) were -1.00 V and -1.37 V *vs.* saturated calomel electrode (SCE) at v 0.1 V s^{-1}, respectively. This clearly indicates that the selenonium salt (**1a**) is reduced much more easily than the sulphur analogue (**7**). Reduction of a saturated solution of salt (**1a**) in acetonitrile with magnesium at room temperature gave a very weak ESR signal, but we were unable to record any hyperfine structure.

Reduction of some Cyclic Onium Salts by Metal.—Selenonium salt (**1a**) was reduced by magnesium metal or zinc–acetic acid to give selenide (**2**) in excellent yield; the reaction mechanisms were different as mentioned above. Therefore, the reduction of some cyclic selenonium and sulphonium salts (**14**), (**22**), (**27**), (**32**) were investigated by four methods: Method A, magnesium (3 mol equiv.) in THF (0.05M-suspension) at room temperature; Method B, magnesium (3 mol equiv.) in THF (0.05M-suspension) at room temperature with sonication; Method C, magnesium (3 mol equiv.)–anthracene–THF complex[12] in THF (0.05M-suspension) at room temperature overnight; Method D, excess of zinc in acetic acid (0.05M-solution) at room temperature. The results are summarised in Table 2. Reduction of the onium salts (**1a**), (**7**), (**14**), and (**22**) by Method C gave inseparable mixtures of their products.

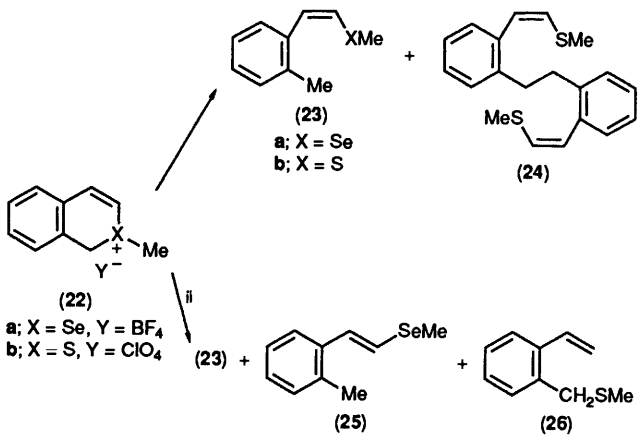
1-Methyl-2*H*-1-benzoseleno(or thio)pyranium salts (**14**) were reduced by Method A or B to give (*Z*)-styrene derivatives (**15**)



Scheme 4. *Reagents:* i, Mg; ii, Zn–AcOH.

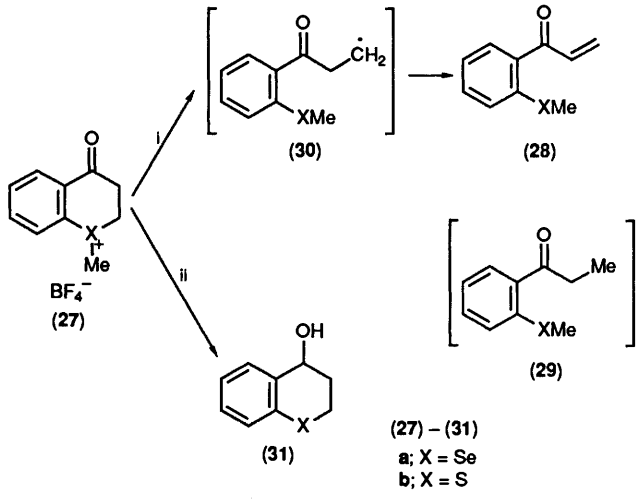
and allylbenzene derivative (**16**) in the quotient (**15**)/(**16**) > 1.5 as shown in Scheme 4 and Table 2 (Entries 1 and 4). On the other hand, reduction of salts (**14**) by Method D afforded compound (**16**) and (*E*)-styrene derivative (**17**) in the quotient (**17**)/(**16**) < 1 (Entries 3 and 6). Selenonium salt (**14a**) or sulphonium salt (**14b**) absorbs a single electron from the metal to form a selenuranyl or a sulphuranyl radical, of which the C–Se or C–S bond is cleaved to give the allyl radical intermediate (resonance structures (**18**) and (**19**). Then the products (**15**) and (**16**) were formed from resonance forms (**18**) and (**19**), respectively, by hydrogen abstraction from the solvent. (*E*)-Styrene derivative (**17**) was not obtained. On the other hand, reduction with zinc–acetic acid yielded the (*E*)-isomer. However, (Z)-styrene derivative (**15**) did not isomerise to (*E*)-(**17**) upon treatment with zinc–acetic acid. This indicates that (*Z*)-allyl anion isomerises to (*E*)-intermediate (**20**) during reduction by Method D.

2-Methyl-1*H*-2-benzoselenopyranium salt (**22a**) was reduced by Method A or B to give (*Z*)-styrene derivative (**23a**) in high yield as shown in Scheme 5 (Entries 7 and 8) while, by Method D, the (*Z*)-styrene (**23a**) and its (*E*)-isomer (**25**) were obtained as an inseparable mixture (Entry 9). (*Z*)-Styrene (**23a**) isomerised on treatment with zinc–acetic acid to (*E*)-isomer (**25**) in 81% yield. Therefore, selenonium salt (**22a**) was reduced to compound (**23a**) followed by isomerisation to compound (**25**) with zinc–acetic acid. 2-Methyl-1*H*-2-benzothiopyranium salt (**22b**) was similarly reduced by Method A or B to give compound (**23b**) and a small amount of dimerised product (**24**) (Entries 10 and 11). Surprisingly, reaction of compound (**22b**) with zinc–acetic acid afforded compound (**23b**) and 2-(methylthiomethyl)styrene (**26**) in 38 and 58% yield, respectively (Entry 12). It is unclear why compound (**26**) was the main product. Treatment of the (*Z*)-styrene sulphur analogue (**23b**) with zinc–acetic acid did not afford its (*E*)-isomer or its [1,5]-rearranged product (**26**), but the substrate (**23b**) was recovered unchanged. Hence, compound (**26**) would be formed by direct cleavage of the S–C(3) bond.



Scheme 5. *Reagents:* i, Mg; ii, Zn–AcOH.

1-Methyl-4-oxo-3,4-dihydro-2*H*-1-benzoseleno(or thio)pyranium salts (**27**) was reduced by Method A or B to give enone derivatives (**28**) as shown in Scheme 6. This reaction proceeded

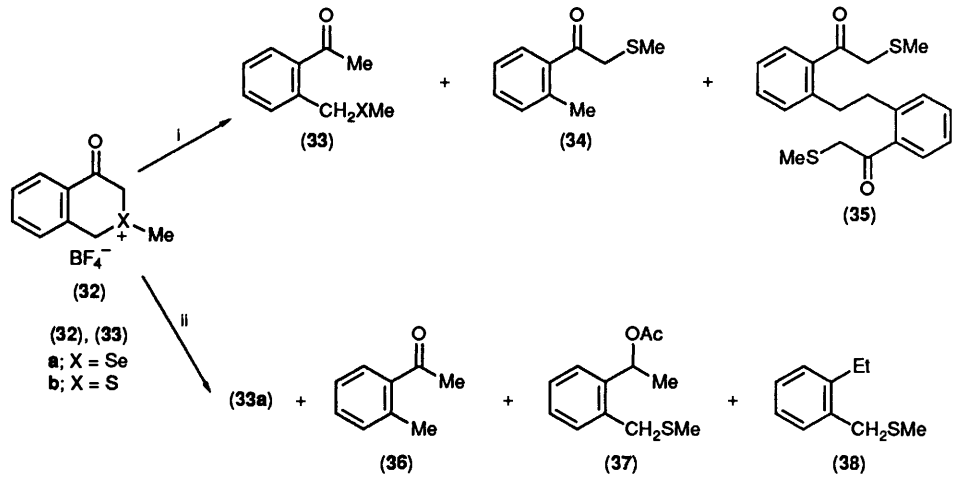


Scheme 6. *Reagents:* i, Mg; ii, Zn–AcOH.

very slowly and unchanged material (**27**) was recovered even after the reaction (Method A) had been allowed to continue for 30 h (Entries 13 and 17). By contrast, the salts (**27**) were smoothly reduced with magnesium activated by anthracene–THF complex (Method C) to give compounds (**28**) in moderate yields, and the other products were complex mixtures (Entries 15 and 19). Since 2-methylseleno(or thio)propiophenone (**29**) was not formed from this reaction, enones (**28**) would not be formed by disproportionation of β-keto radicals (**30**). Reaction under deoxygenated conditions afforded traces of enones (**28**) and a complex mixture of other products. Therefore, oxygen dissolved in the solvent would participate in enone formation, but the detailed mechanism is unclear. On the other hand, reduction of salts (**27**) by Method D afforded 4-hydroxy-3,4-dihydro-2*H*-1-benzoseleno(or thio)pyran (**31a** or **b**) in low yield and unidentified polymers (Entries 16 and 20).

Both the onium and the carbonyl groups were reduced with zinc–acetic acid and demethylation was faster than ring opening.

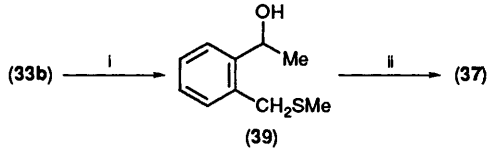
2-Methyl-4-oxo-3,4-dihydro-1*H*-2-benzoselenopyranium salt (**32a**) was reduced by Method A or B to give 2-(methylselenomethyl)acetophenone (**33a**) as a single product as shown in Scheme 7 (Entries 21 and 22). However, reduction by Method D yielded compound (**33a**) (82%) and 2-methyl-



Scheme 7. *Reagents:* i, Mg; ii, Zn–AcOH.

acetophenone (**36**) (16%) (Entry 24). The latter would be formed by deselenation of the former under the reaction conditions. The reaction with zinc in refluxing acetic acid gave the acetophenone (**36**) in quantitative yield. Both reactions with zinc did not give any product derived from reduction of the carbonyl group. On the other hand, the corresponding sulphonium salt (**32b**) was reduced by Method A, B or C to give 2-(methylthiomethyl)-acetophenone (**33b**), 2-methyl-α-(methylthio)acetophenone (**34**) and a dimer (**35**) (Entries 25–27). The structure of these products was established by their NMR spectra. The ^{13}C NMR spectrum of the sulphide (**33b**) showed the methyl carbon of the acetyl group and the methylene carbon at δ_C 29.7 and 36.1, respectively. The ^{13}C NMR spectrum of the sulphide (**34**) exhibited the 2-methyl and the methylene carbons at δ_C 21.4 and 42.4, respectively. The ^1H NMR spectrum of compound (**35**) showed the benzylic methylene protons and other methylene protons adjacent to the carbonyl group at δ 3.38 and 3.95, respectively: the former was shifted 0.3 ppm downfield from the corresponding signal of the methylene protons of compound (**33b**), and the latter appeared in almost the same place as that of compound (**34**).

Reduction of the salt (**32b**) by zinc–acetic acid afforded unexpected products (**37**) and (**38**) (Entry 28), but reduction under reflux conditions afforded the ethylbenzene derivative (**38**) in low yield without the acetate (**37**). Treatment of acetophenone derivative (**33b**) with zinc–acetic acid gave acetate (**37**) in only 5% yield. Therefore, the carbonyl group of sulphonium salt (**32b**) was reduced first and then the sulphonium moiety. The structure of compound (**37**) was established by an alternative synthesis as shown in Scheme 8.



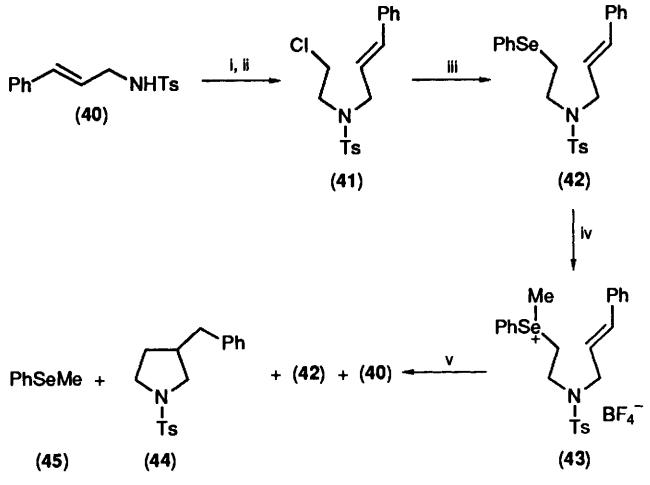
Scheme 8. *Reagents:* i, $NaBH_4$; ii, AcCl, pyridine.

Acetophenone derivative (**33b**) was reduced by sodium borohydride to give the alcohol (**39**), which was acetylated to give compound (**37**) in high yield.

The difference in the reactions of compounds (**32a**) and (**32b**) with zinc–acetic acid is attributable to the affinity of zinc for selenium and sulphur and to the strength of C–X (X = S, Se) bonds. The reductive C(3)–X bond cleavage of β-keto onium salts (**32**) is markedly different from the C(1)–X bond cleavage of other salts (**1**), (**7**), (**22**). The benzoyl methyl radical generated by the C(3)–X bond cleavage would be stabilised by the α-carbonyl group.[13] This makes C(3)–X bond cleavage easy. C(3)–Se bond cleavage occurred exclusively in the selenonium salt (**32a**), while C(1)–S bond cleavage occurred to a considerable extent in the sulphonium salt (**32b**). This difference may be attributed to the difference in ring-strain or in configuration between the $ArCOCH_2$ and the $ArCH_2$ ligands of the selenuranyl and the sulphuranyl radicals. More chemical evidence is necessary to clarify this subject.

We conclude that the selenonium salts are reduced by metallic reagents more readily than are the corresponding sulphonium salts and the products are given in high yield without the formation of by-products. Reduction with magnesium predominates over that with other reducing agents. In particular, magnesium activated by sonication reduced onium salts in a short time and in high yield, and did not reduce the carbonyl group.

Application to Cyclisation Reaction.—Onium salts were reduced by a metal to form carbon radical intermediates *via* selenuranyl (or sulphuranyl) radicals. We investigated the utilisation of such radicals for the cyclisation reaction shown in Scheme 9. *N*-[(*E*)-Cinnamyl]toluene-*p*-sulphonamide (**40**) was treated with 1-bromo-2-chloroethane in the presence of base to



Scheme 9. *Reagents:* i, NaH; ii, $BrCH_2CH_2Cl$; iii, PhSeNa; iv, MeI, $AgBF_4$; v, Mg, sonication.

give *N*-[(*E*-cinnamyl]-*N*-(2-chloroethyl)toluene-*p*-sulphonamide (**41**) in 51% yield. Reaction of compound (**41**) with sodium benzeneselenolate gave *N*-[(*E*)-cinnamyl]-*N*-[2-(phenylseleno)ethyl]toluene-*p*-sulphamide (**42**) in 95% yield. Compound (**42**) was then methylated by methyl iodide and silver tetrafloroborate to give a selenonium salt (**43**) in 61% yield. Attempted phenylation of compound (**42**) by diphenyliodonium tetrafluoroborate in the presence of copper catalyst was unsuccessful. Selenonium salt (**43**) was treated with magnesium metal by sonication for 30 min to give a pyrrolidine derivative (**44**) (11%), methylselenobenzene (**45**) (7%), demethylated product (**42**) (52%), and a decomposition product (**40**) (2%). This result shows that regioselective cleavage of the C–Se bond is important for application of this methodology to organic synthesis. We are now studying new developments of C–Se or C–S bond cleavage *via* radicals.[14]

Experimental

M.p.s were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra of solids (KBr) and liquids (film) were recorded on a JASCO IRA-100 spectrophotometer. ^{1}H NMR spectra were obtained for solutions in $CDCl_3$ on a Hitachi R20-B (60 MHz) or a JEOL GX-270 (270 Hz) spectrometer with tetramethylsilane as internal standard, unless otherwise indicated. ^{13}C Spectra were run on a JEOL GX-270 spectrometer. Mass spectra were obtained using a JEOL JMS-D 300 spectrometer with a direct-insertion probe at 70 eV. All exact-mass determination was obtained on a JMA 2000 on-line system. Ultrasonic irradiation was provided by a Branson B-220 ultrasound cleaner (45 kHz, 100 W). All liquid products were purified by preparative TLC (PLC) and then submitted to elemental analyses.

General Procedure for the Reactions of (**1**) *with Grignard Reagents.*—Grignard reagent (3 mmol) was prepared from the corresponding alkyl halide (3 mmol) and magnesium (3 mmol) in THF (20 ml). Selenonium salt (**1**) (300 mg, 1 mmol) was added to the solution and the mixture was stirred. Saturated aq. ammonium chloride was carefully added to the reaction mixture at 0 °C and the mixture was extracted with diethyl ether. The extract was washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was separated by PLC [silica gel; hexane–dichloromethane (5:1)]. Reaction conditions and yields of products are summarised in Table 1.

2-[2-(Methylseleno)ethyl]toluene (**2**), pale yellow oil; δ_H 2.03 (3 H, s, SeMe), 2.56 (3 H, s, ArMe), 2.70–2.76 (2 H, m, CH_2), 2.88–3.02 (2 H, m, CH_2) and 7.14 (4 H, s, ArH) (Found: M^+, 214.0246; C, 56.1; H, 6.7. Calc. for $C_{10}H_{14}Se$: *M*, 214.0259; C, 56.3; H, 6.6%). 3,4-Dihydro-1*H*-2-benzoselenopyran (**3**) was identical (^{1}H NMR and mass) with an authentic specimen.[15]

Reaction of Compound (**1a**) *with Butyl-lithium.*—A solution of butyl-lithium in hexane (1.5 mmol) was added to a suspension of the salt (**1a**) (300 mg, 1 mmol) in THF (20 ml) at −78 °C. The temperature was gradually raised to ambient and the mixture was stirred for 12 h. Saturated aq. ammonium chloride was added to the mixture and the whole was extracted with diethyl ether. The extract was washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was separated by PLC [silica gel; hexane–dichloromethane (5:1)].

1,2-*Bis*-{2-[2-(*methylseleno*)*ethyl*]*phenyl*}*ethane* (**4**) (29 mg, 13%), pale yellow oil; δ_H 1.98 (6 H, s, Me × 2), 2.50–3.25 (12 H, m, CH_2 × 6) and 7.18 (8 H, br s, ArH) (Found: M^+, 426.0363. $C_{20}H_{26}Se_2$ requires *M*, 426.0333).

1-(2-*Ethenylphenyl*)-2-{2-[2-(*methylseleno*)*ethyl*]*phenyl*}-*ethane* (**5**) (24 mg, 16%), pale yellow oil; δ_H 1.98 (3 H, s, Me), 2.50–3.25 (8 H, m, CH_2 × 4), 5.35 (1 H, dd, *J* 10.5, 1.5 Hz, =C*H*H), 5.68 (1 H, dd, *J* 17.3, 1.5 Hz, =CH*H*) and 6.80–7.70 (9 H, m, CH and ArH) (Found: M^+, 330.0874. $C_{19}H_{22}Se$ requires *M*, 330.0886). Compound (**2**) was identical (^{1}H NMR and mass) with an authentic specimen.

Reaction of Compound (**1a**) *with Tributyltin Hydride.*—Tributyltin hydride (306 mg, 1 mmol) was added to a suspension of compound (**1a**) (300 mg, 1 mmol) and AIBN (16 mg, 0.1 mmol) in benzene (20 ml) under nitrogen and the mixture was refluxed for 1 h. 10% aq. potassium fluoride was added to the mixture and the whole was extracted with benzene. The extracts were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was separated by PLC [silica gel; hexane–dichloromethane (5:1)] to give compound (**2**) (113 mg, 52%). This product was identical (^{1}H NMR and mass) with an authentic specimen.

Reaction of Compound (**1a**) *with LAH.*—Selenonium salt (**1a**) (300 mg, 1 mmol) was added to a suspension of LAH (50 mg, 1.3 mmol) in THF (20 ml) and the mixture was stirred for 18 h at room temperature. A small amount of ethyl acetate was added until generation of hydrogen gas ceased and then water was added to the mixture. The whole was extracted with diethyl ether. The extracts were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was separated by PLC [silica gel; hexane–dichloromethane (5:1)] to give compounds (**2**) (42 mg, 20%), (**3**) (101 mg, 50%), and (**4**) (50 mg, 24%). Each product was identical (^{1}H NMR and mass) with an authentic specimen.

Reaction of Compound (**1a**) *with Sodium Borohydride.*—Sodium borohydride (38 mg, 1 mmol) was added to a solution of compound (**1a**) (300 mg, 1 mmol) in ethanol (20 ml) and the mixture was refluxed for 30 min. The mixture was poured into water and extracted with dichloromethane. The extracts were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was separated by PLC [silica gel; hexane–dichloromethane (5:1)] to give compounds (**2**) (107 mg, 50%) and (**3**) (23 mg, 12%). Each product was identical (^{1}H NMR and mass) with an authentic specimen.

General Procedure for the Reactions of Onium Salts (**1**), (**7**), (**14**), (**22**), (**27**), and (**32**) *with Magnesium Metal* (*Method A*).—Magnesium turnings (73 mg, 3 mmol) were added to a suspension of an onium salt (1 mmol) in dry THF (20 ml) and the mixture was stirred for 30 h at room temperature. Saturated aq. ammonium chloride (10 ml) was added to the mixture and then the whole was extracted with dichloromethane. The extract was washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was separated by PLC on silica gel. Yields of products are listed in Tables 1 and 2.

2-[2-(*Methylthio*)*ethyl*]*toluene* (**8**), an oil; δ_H 2.10 (3 H, s, SMe), 2.30 (3 H, s, ArMe), 2.48–3.08 (4 H, m, CH_2CH_2) and 7.17 (4 H, s, ArH) (Found: M^+, 166.0819. $C_{10}H_{14}S$ requires *M*, 166.0817).

1-*Methylseleno*-2-(*prop*-1-*enyl*)*benzene* (**15a**) and 1-*allyl*-2-*methylselenobenzene* (**16a**) were obtained as an inseparable mixture and their yields were calculated by the integral intensities of their Se-methyl signals in the ^{1}H NMR spectrum; δ_H (**15a**) 1.75 (3 H, dd, *J* 8.8, 2.0 Hz, Me), 2.27 (3 H, s, Me), 5.81–5.95 (1 H, m, CH), 6.49 (1 H, dd, *J* 8.8, 1.5 Hz, ArC*H*) and 7.12–7.36 (4 H, m, ArH); (**16a**) 2.29 (3 H, s, Me), 3.49 (2 H, d, *J* 6.8 Hz, ArCH_2), 5.02–5.11 (2 H, m, CH_2), 5.98–6.04 (1 H, m, CH) and

7.12–7.36 (4 H, m, ArH) (Found: M^+, 212.0094; C, 57.15; H, 5.75. $C_{10}H_{12}Se$ requires M, 212.0103; C, 57.4; H, 5.8%).

1-Methylthio-2-(prop-1-enyl)benzene (**15b**) and 1-allyl-2-methylthiobenzene (**16b**) were obtained as an inseparable mixture and their yields were calculated from the integral intensities of their *S*-methyl signals in the ^1H NMR spectrum. Compounds (**15b**) and (**16b**) were identical (^1H NMR and mass) with authentic specimens.[16]

(Z)-2-[2-(*Methylseleno*)*ethenyl*]*toluene* (**23a**), pale yellow oil; δ_H 2.12 (3 H, s, Me), 2.25 (3 H, s, Me), 6.60 (1 H, d, *J* 9.8 Hz, CH), 6.93 (1 H, d, *J* 9.8 Hz, ArC*H*) and 7.03–7.58 (4 H, m, ArH) (Found: M^+, 212.0094; C, 57.4; H, 5.8. $C_{10}H_{12}Se$ requires M, 212.0103; C, 57.4; H, 5.8%).

(Z)-2-[2-(*Methylthio*)*ethenyl*]*toluene* (**23b**), pale yellow oil; δ_H 2.30 (3 H, s, Me), 2.35 (3 H, s, Me), 6.26 (1 H, d, *J* 10.5 Hz, CH), 6.55 (1 H, d, *J* 10.5 Hz, ArC*H*), 7.14–7.25 (3 H, m, ArH) and 7.50–7.53 (1 H, m, ArH) (Found: M^+, 164.0656. $C_{10}H_{12}S$ requires M, 164.0659).

1,2-*Bis*-{2-[2-(*methylthio*)*ethenyl*]*phenyl*}*ethane* (**24**), an oil; δ_H 2.35 (6 H, s, Me × 2), 2.86 (4 H, s, ArCH_2 × 2), 6.25 (2 H, d, *J* 10.5 Hz, CH × 2), 6.58 (2 H, d, *J* 10.5 Hz, ArC*H* × 2), 7.14–7.26 (6 H, m, ArH) and 7.49–7.52 (2 H, m, ArH) (Found: M^+, 326.1185. $C_{20}H_{22}S_2$ requires M, 326.1164).

2-(*Methylseleno*)*phenyl vinyl ketone* (**28a**), brown oil; ν_{max}(film) 1660 cm^{-1} (CO); δ_H 1.98 (3 H, s, Me), 5.89 (1 H, dd, *J* 10.5, 2.2 Hz, =C*H*H), 6.36 (1 H, dd, *J* 16.5, 2.2 Hz, =CH*H*) and 6.91–8.00 (5 H, m, CH and ArH) (Found: M^+, 225.9914; C, 53.5; H, 4.7. $C_{10}H_{10}OSe$ requires M^+, 225.9896; C, 53.35; H, 4.5%).

2-(*Methylthio*)*phenyl vinyl ketone* (**28b**), orange oil; ν_{max}(film) 1660 cm^{-1} (CO); δ_H 2.44 (3 H, s, Me), 5.95 (1 H, dd, *J* 12.2, 0.5 Hz, =C*H*H), 6.29 (1 H, dd, *J* 18.6, 0.5 Hz, =CH*H*), 6.97 (1 H, m, CH) and 7.35–7.67 (4 H, m, ArH) (Found: M^+, 178.0441. $C_{10}H_{10}OS$ requires M, 178.0452).

2-(*Methylselenomethyl*)*acetophenone* (**33a**), brown oil; ν_{max} 1685 cm^{-1} (CO); δ_H 1.89 (3 H, s, Me), 2.58 (3 H, s, Me), 4.03 (2 H, s, CH_2), 7.00–7.45 (3 H, m, ArH) and 7.57–7.83 (1 H, m, ArH); δ_C 4.5 (q), 26.8 (t), 29.5 (q), 126.6 (d), 129.9 (d), 131.1 (d), 131.2 (d), 136.5 (s), 140.4 (s) and 201.6 (s) (Found: M^+, 228.0070; C, 53.0; H, 5.4. $C_{10}H_{12}OSe$ requires M, 228.0054; C, 52.9; H, 5.3%).

2-(*Methylthiomethyl*)*acetophenone* (**33b**), pale yellow oil; ν_{max}(film) 1680 cm^{-1} (CO); δ_H 2.08 (3 H, s, Me), 2.55 (3 H, s, Me), 4.01 (2 H, s, CH_2), 7.23–7.42 (3 H, m, ArH) and 7.36–7.70 (1 H, m, ArH); δ_C 15.3 (q), 29.7 (q), 36.1 (t), 126.9 (d), 129.4 (d), 131.1 (d), 131.2 (d), 137.7 (s), 138.6 (s) and 202.1 (s) (Found: M^+, 180.0601; C, 66.4; H, 6.8. $C_{10}H_{12}OS$ requires M, 180.0608; C, 66.6; H, 6.7%).

2-*Methyl*-α-(*methylthio*)*acetophenone* (**34**), pale yellow oil; ν_{max} 1680 cm^{-1} (CO); δ_H 2.07 (3 H, s, Me), 2.60 (3 H, s, Me), 3.72 (2 H, s, CH_2), 7.27–7.44 (3 H, m, ArH) and 7.67–7.69 (1 H, m, ArH); δ_C 15.9 (q), 21.2 (q), 41.9 (t), 125.6 (d), 128.7 (d), 131.5 (d), 132.0 (d), 136.2 (s), 139.1 (s) and 197.7 (s) (Found: M^+, 180.0618. C, 66.7; H, 6.8. $C_{10}H_{12}OS$ requires: M, 180.0601; C, 66.6; H, 6.7%).

2,2′-*Bis*(*methylthio*)-1,1′-*ethylenedi*(o-*phenylene*)*diethanone* (**35**), as plates; m.p. 101–102 °C (decomp.); ν_{max} 1665 cm^{-1} (CO); δ_H 2.11 (6 H, s, Me × 2), 3.38 (4 H, s, CH_2 × 2), 3.95 (4 H, s, CH_2 × 2), 7.26–7.45 (6 H, m, ArH) and 7.80–7.84 (2 H, m, ArH); δ_C 15.3 (q), 29.7 (t), 36.0 (t), 127.1 (d), 128.9 (d), 130.9 (d), 131.1 (d), 138.1 (s) and 203.2 (s); *m*/*z* 358 (M^+) [Found: (M − MeSH), 310.1033. $C_{19}H_{18}O_2S$ requires *m*/*z*, 310.1027]. Compound (**35**) gradually decomposed on recrystallisation and successful elemental analysis data could not be obtained. In the mass spectrum, its M^+ peak at *m*/*z* 358 was too small to be measured accurately.

General Procedure for the Reaction of Onium Salts (**1**), (**7**), (**14**), (**22**), (**27**) *and* (**32**) *with Magnesium under Ultrasonic Irradiation* (*Method B*).—Magnesium (73 mg, 3 mmol) was added to a suspension of an onium salt (1 mmol) in THF (20 ml) and the mixture was sonicated under nitrogen at room temperature. Saturated aq. ammonium chloride was added to the mixture and the whole was extracted with diethyl ether. The extract was washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was separated by PLC [silica gel; hexane–dichloromethane (5:1–1:1)]. The reaction conditions and yields of all products are summarised in Tables 1 and 2. Each product was identical (^1H NMR and mass) with an authentic specimen obtained by Method A.

General Procedure for the Reaction of Onium Salts (**27**) *and* (**32**) *with Magnesium–Anthracene–THF Complex* (*Method C*).—Magnesium (73 mg, 3 mmol) was added to a solution of anthracene (534 mg, 3 mmol) in THF (20 ml) and the mixture was refluxed under nitrogen for 3 h. An onium salt (1 mmol) was added to the cooled mixture and the resulting mixture was stirred under nitrogen for 12 h. Saturated aq. ammonium chloride was added to the mixture and the whole was extracted with diethyl ether. The extract was washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was recrystallised from ether–hexane to give anthracene. The filtrate was evaporated and the residue was separated by PLC [silica gel; hexane–dichloromethane (5:1–1:1)]. The yields of products are summarised in Table 2. Each product was identical (^1H NMR and mass) with an authentic specimen obtained by Method A.

General Procedure for the Reactions of Onium Salts (**1**), (**7**), (**14**), (**22**), (**27**) *and* (**32**) *with Zinc in Acetic Acid* (*Method D*).—Zinc powder (3 g) activated by 5% hydrochloric acid was added to a solution of an onium salt (1 mmol) in acetic acid (20 ml) and the mixture was stirred under nitrogen for 12 h. The mixture was poured into water (100 ml) and filtered. The filtrate was extracted with dichloromethane. The extract was washed successively with water and saturated aq. sodium hydrogen carbonate, and then dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was separated by PLC [silica gel; hexane–dichloromethane (5:1–1:1)]. Products and their yields are summarised in Tables 1 and 2.

2-[(*E*)-2-(Methylseleno)ethenyl]toluene (**25**) was obtained as an inseparable mixture with its *Z*-isomer (**23a**) and its yield was calculated from the integral intensities of its Se-methyl signal in the ^1H NMR spectrum. δ_H 1.91 (3 H, s, Me), 2.27 (3 H, s, Me), 6.80 (1 H, d, *J* 15.6 Hz, =CH), 6.95 (1 H, d, *J* 15.6 Hz, =CH), 7.10–7.20 (3 H, m, ArH) and 7.34–7.39 (1 H, m, ArH); *m*/*z* 212 (M^+).

2-(*Methylthiomethyl*)*styrene* (**26**), pale yellow oil; δ_H 2.00 (3 H, s, Me), 3.78 (2 H, s, CH_2), 5.26 (1 H, dd, *J* 10.0, 2.0 Hz, =C*H*H), 5.62 (1 H, dd, *J* 16.0, 2.0 Hz, =C*H*H), and 6.83–7.67 (5 H, m, =CH and ArH) (Found: M^+, 164.0657. $C_{10}H_{12}S$ requires M, 164.0659).

3,4-Dihydro-2*H*-1-benzoselenopyran-4-ol (**31a**)[17] and 3,4-dihydro-2*H*-1-benzothiopyran-4-ol (**31b**)[18] were identical (^1H NMR and mass) with authentic specimens.

2-Methylacetophenone (**36**) was also identical (^1H NMR and IR) with a commercially available sample.

1-[2-(*Methylthiomethyl*)*phenyl*]*ethyl acetate* (**37**), an oil; ν_{max}(film) 1730 and 1250 cm^{-1} (ester); δ_H 1.57 (3 H, d, *J* 6.5 Hz, Me), 2.03 (3 H, s, Me), 2.04 (3 H, s, Me), 3.65 (1 H, d, *J* 13.0 Hz, C*H*H), 4.02 (1 H, d, *J* 13.0 Hz, CH*H*), 7.18–7.31 (3 H, m, ArH) and 7.44–7.47 (1 H, m, ArH); δ_C 15.3 (q), 21.2 (q), 22.1 (q), 35.5 (t), 68.4 (d), 126.5 (d), 127.4 (d), 127.6 (d), 130.1 (d), 134.8 (s), 140.4 (s) and 170.2 (s); *m*/*z* 195 (M − AcOH) (Found: C, 64.0; H, 7.2; $C_{12}H_{16}O_2S$ requires C, 64.25; H, 7.2%).

1-*Ethyl*-2-(*Methylthiomethyl*)*benzene* (**38**), pale yellow oil; δ_H 1.25 (3 H, t, *J* 7.5 Hz, Me), 2.03 (3 H, s, Me), 2.75 (2 H, q, *J* 7.5 Hz, CH_2), 3.68 (2 H, s, CH_2) and 7.18 (4 H, br s, ArH) (Found: M^+, 166.0805. $C_{10}H_{14}S$ requires *M*, 166.0815).

Reduction of Compound (**1a**) *with Magnesium in* [$^2H_8$]*THF*.—A suspension of the salt (**1a**) (50 mg) and magnesium (12 mg) in [$^2H_8$]THF (1 ml) was sonicated under nitrogen at room temperature for 30 min. An aliquot of the reaction mixture was filtered, and evaporated under reduced pressure. The ^1H NMR and mass spectra of the residue were measured. The spectral evidence indicated that the product was 2-[2-(*methylseleno*)*ethyl*][α-$^2H_1$]*toluene* (**9**), δ_H(270 MHz, $CDCl_3$) 2.03 (3 H, s, SeMe), 2.31 (2 H, t, *J* 2.0 Hz, CH_2D), 2.75 (2 H, t, *J* 8.5 Hz, CH_2), 2.98 (2 H, *J* 8.5 Hz, CH_2) and 7.15 (4 H, s, ArH); *m/z* 215 (M^+, 22%) and 120 (*M* − SeMe, 100).

Reduction of the Salt (**1a**) *with Zinc in Acetic* [$^2H_1$]*Acid*.—A suspension of compound (**1a**) (100 mg) and zinc powder (1 g) in acetic [$^2H_1$]acid (3 ml) was stirred overnight under nitrogen at room temperature. The reaction mixture was poured into water and the precipitate was filtered off, and washed with dichloromethane. The filtrate was extracted with dichloromethane. The washings and the extracts were combined, washed with water, dried ($MgSO_4$) and evaporated. The residue was separated by PLC to give the deuteriated product (**9**) (72 mg, 58%), which was identical with the product obtained from the reduction of compound (**1a**) with magnesium in [$^2H_8$]THF in all respects (^1H NMR and mass spectra).

1-[2-(*Methylthiomethyl*)*phenyl*]*ethanol* (**39**).—Sodium borohyride (42 mg, 1.1 mmol) was gradually added to a solution of compound (**33b**) (202 mg, 1.1 mmol) in ethanol (5 ml) and the mixture was stirred for 4 h at room temperature, poured into water, and extracted with dichloromethane. The extract was washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was separated by PLC [silica gel; hexane–dichloromethane (3:1)] to give the alcohol (**39**) (177 mg, 87%) as an oil; ν_{max} 3450 cm^{-1} (OH); δ_H 1.50 (3 H, d, *J* 6 Hz, Me), 2.00 (3 H, s, Me), 2.52 (1 H, br s, OH), 3.72 (2 H, s, CH_2), 5.20 (1 H, q, *J* 6 Hz, CH), and 7.00–7.65 (4 H, m, ArH); *m/z* 164 (*M* − H_2O).

1-[2-(*Methylthiomethyl*)*phenyl*]*ethyl Acetate* (**37**).—Acetyl chloride (0.05 ml, 0.7 mmol) was added to a solution of the alcohol (**39**) (128 mg, 0.7 mmol) and pyridine (0.11 ml, 1.4 mmol) in dichloromethane (2 ml) at 0 °C. The mixture was stirred for 12 h, then washed successively with water and 10% aq. hydrochloric acid and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was separated by PLC [silica gel; hexane–dichloromethane (3:2)] to give the acetate (**37**) (140 mg, 89%). This sample was identical (^1H NMR and IR) with an authentic specimen.

N-(2-*Chloroethyl*)-N-[(E)-*cinnamyl*]*toluene*-p-*sulphonamide* (**41**).—*N*-Cinnamyltoluene-*p*-sulphonamide (**40**) (3 g, 10 mmol) was added to a suspension of sodium hydride (300 mg, 12.5 mmol) in DMF (50 ml) and the mixture was stirred for 15 min at room temperature. A solution of 1-bromo-2-chloroethane (2.25 g, 16 mmol) in DMF (45 ml) was gradually added to the suspension during 30 min. The resulting mixture was stirred overnight, then poured into water and extracted with benzene–hexane (4:1). The extracts were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was separated by column chromatography [silica gel; hexane–ethyl acetate (5:1)] to give *compound* (**41**) (1.85 g, 51%) as a pale yellow oil; ν_{max} 1155 and 1340 cm^{-1} (SO_2); δ_H 2.42 (3 H, s, Me), 3.43 (2 H, t, *J* 7.0 Hz, CH_2), 3.64 (2 H, t, *J* 7.0 Hz, CH_2), 3.99 (2 H, dd, *J* 6.8, 1.0 Hz, CH_2), 5.95 (1 H, m, =CH), 6.47 (1 H, d, *J* 16.1 Hz, =CH), 7.20–7.32 (7 H, m, ArH) and 7.73 (2 H, d, *J* 8.3 Hz, ArH) (Found: M^+, 349.0926; C, 61.6; H, 5.8; N, 4.0. $C_{18}H_{20}ClNOS$ requires *M*, 349.0904; C, 61.8; H, 5.8; N, 4.0%).

N-[(E)-*Cinnamyl*]-N-[2-(*phenylseleno*)*ethyl*]*toluene*-p-*sulphonamide* (**42**).—Alkyl chloride (**41**) (2 g, 5.7 mmol) was added to a solution of sodium benzeneselenolate prepared from diphenyl diselenide (930 mg, 2.9 mmol) and sodium borohydride (216 mg, 5.7 mmol) in ethanol (30 ml). The mixture was refluxed for 1 h, then poured into water and extracted with dichloromethane. The extracts were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was separated by PLC [silica gel; hexane–ethyl acetate (5:1)] to give the *selenide* (**42**) (2.56 g, 95%) as a pale yellow oil; ν_{max} 1160 and 1340 cm^{-1} (SO_2); δ_H 2.39 (3 H, s, Me), 3.01–3.08 (2 H, m, CH_2), 3.31–3.36 (2 H, m, CH_2), 3.90 (2 H, d, *J* 6.9 Hz, CH_2), 5.90–6.01 (1 H, m, =CH), 6.30 (1 H, d, *J* 16.1 Hz, =CH), 7.08–7.42 (12 H, m, ArH) and 7.63 (2 H, d, *J* 8.3 Hz, ArH); *m/z* 471 (M^+) (Found: C, 61.2; H, 5.5; N, 3.1. $C_{24}H_{25}NO_2SSe$ requires C, 61.3; H, 5.4; N, 3.0%).

2-{N-[(E)-*Cinnamyl*]-N-p-*tosylamino*}*ethyl*(*methyl*)-*phenylselenonium Tetrafluoroborate* (**43**).—Silver tetrafluoroborate was added to a solution of the selenide (**42**) (1 g, 2 mmol) and iodomethane (1.4 g, 10 mmol) in dichloromethane (10 ml) at 0 °C and the mixture was stirred overnight. The precipitate was filtered off, and washed with acetonitrile. The filtrate and washings were combined and the solvent was removed under reduced pressure. The residue was rinsed with ethanol and dried *in vacuo* to give the *salt* (**43**) (1.2 g, 61%) as a pale yellow oil; ν_{max} 1060 (BF_4), and 1155 and 1340 cm^{-1} (SO_2); δ_H 2.41 (3 H, s, Me), 3.13 (3 H, s, Me), 3.52–3.60 (1 H, m, CH*H*), 3.80–3.95 (4 H, m, CH_2 × 2), 4.13–4.19 (1 H, m, C*H*H), 5.71–5.79 (1 H, m, =CH), 6.51 (1 H, d, *J* 15.6 Hz, =CH), 7.18–7.32 (7 H, m, ArH), 7.52–7.57 (5 H, m, ArH) and 7.80–7.85 (2 H, m, ArH) (Found: C, 52.25; H, 4.9; N, 2.5. $C_{25}H_{28}BF_4NO_2SSe$ requires C, 52.5; H, 4.9; N, 2.45%).

Reaction of Selenonium Salt (**43**) *with Magnesium*.—Magnesium (50 mg, 2 mmol) was added to a solution of compound (**43**) (320 mg, 0.56 mmol) in THF (3 ml) and the mixture was sonicated under nitrogen for 30 min at room temperature. A saturated solution of ammonium chloride was added to the mixture and the whole was extracted with diethyl ether. The extracts were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was separated by PLC [silica gel; hexane–ethyl acetate (5:1)] to give compound (**40**) (4 mg, 2.5%), compound (**42**) (137 mg, 52%), 3-benzyl-*N*-*p*-tosylpyrrolidine (**44**)[19] (20 mg, 11%), and methylselenobenzene (**45**)[20] (7 mg, 7%). Each product was identical (^1H NMR, IR and mass) with an authentic specimen.

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