Cyclic Selenonium *exo*-Ylides (3,4-Dihydro-1*H*-2-benzoselenin-2-io)methanides; Syntheses and Reactions

Mikio Hori,* Tadashi Kataoka, Hiroshi Shimizu, Kazuhiro Tsutsumi, Yong-Zhou Hu, and Motoo Nishigiri
Gifu Pharmaceutical University, 5-6-1, Mitahora-higashi, Gifu 502, Japan

Stable cyclic selenonium *exo*-ylides (3,4-dihydro-1*H*-2-benzoselenin-2-io)methanides; (**5a—e**) have been synthesized by reactions of 3,4-dihydro-1*H*-2-benzoselenin2,2-dichloride (**4**) or *N*-(3,4-dihydro-1*H*-2-benzoselenin-2-io)toluene-*p*-sulphonamidate (**6**) and active methylene compounds. The ylidic nature and the stable configuration of (**5a—e**) were established on the basis of their spectral data. The reactions of ylides having acetyl group(s) (**5a,b**) with dimethyl acetylenedicarboxylate afforded the furan derivatives (**8a,b**) and (**9a**) and the dihydrobenzoselenin (**3**), while reactions of the ylides having no acetyl group, (**5c—e**), afforded the benzoselenonines (**14c—e**). The diacetylmethanide (**5a**) when heated gave the benzoselenepine (**15**), while (**5c**) when heated afforded the styrene derivative (**18**) and a tetrasubstituted ethylene (**19**). When heated, (**5d**) gave the [1,2] rearranged product (**22**). 3,4-Dihydro-1*H*-2-benzoselenin-2-io)phenacylide (**31**) was generated by the reaction of the selenonium salt (**24**) with sodium hydride but was too unstable to be isolated. Thermal decomposition of (**31**) yielded (**3**), its counterparts (**26—28**), a styrene derivative (**25**), and a novel rearrangement product (**29**).

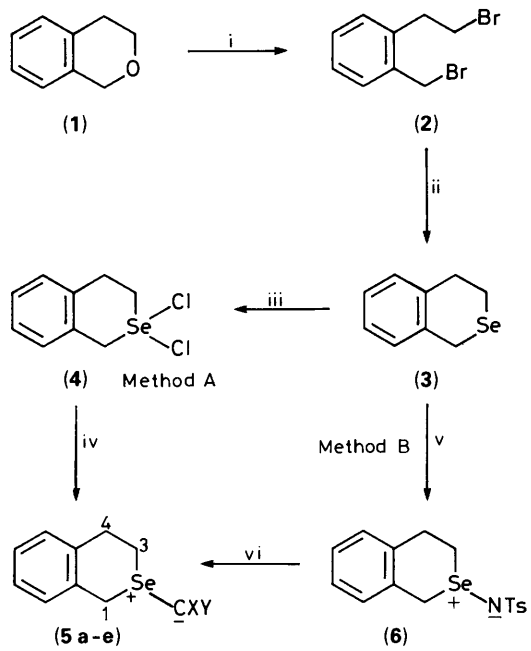
Previously, we reported on the reactivity of a cyclic selenonium *endo*-ylide, 2-methyl-4-oxo-3,4-dihydro-1*H*-2-benzoselenin-2-io-3-ide.[1] Although this compound is unstable, in spite of containing an electron-withdrawing group, the corresponding sulphonium ylide is stable and its reactivity has been investigated.[2] The instability of the cyclic selenonium ylide is ascribed to ring-strain and the weak C–Se bond,[3] the sterically less hindered acyclic selenonium ylides showing a similar reactivity to the sulphur analogues.[4,5]

Here, we describe the syntheses and the reactions of the cyclic *exo*-ylides, 3,4-dihydro-1*H*-2-benzoselenin-2-io)methanides (**5**), the character of which is intermediate between cyclic and acyclic selenonium ylides.

Results and Discussion

Syntheses of Selenonium Ylides (**5**).—The parent compound for the ylides (**5**), 3,4-dihydro-1*H*-2-benzoselenin (**3**), was synthesized by Holliman and Mann[6] by a time-consuming method from relatively inaccessible reagents. Our improved method is shown in Scheme 1. The 2-benzopyran (**1**) was allowed to react with 47% hydrobromic acid in the presence of a phase-transfer catalyst, tributyl(cetyl)phosphonium bromide to give 2-(2-bromoethyl)benzyl bromide (**2**) (70%). The latter when treated with sodium selenide (prepared from selenium powder and sodium borohydride) gave the dihydro-2-benzoselenin (**3**) (70%) and this with sulphuryl chloride at −30 °C afforded the 2,2-dichloride (**4**) (94%). Treatment of the latter with a 2 molar equiv. of the anions of active methylene compounds gave the ylides (**5a—e**) (Method A).[7] If the selenide (**3**) was allowed to react with chloramine T trihydrate at room temperature the sulphonamidate (**6**) was obtained (68%). The ^{1}H n.m.r. spectrum of the latter showed signals similar to those of the ylides (**5**). With 5 molar equiv. of active methylene compounds the sulphanomidate (**6**) gave the ylides (**5a—e**) (Method B).[8] The above synthetic routes are shown in Scheme 1.

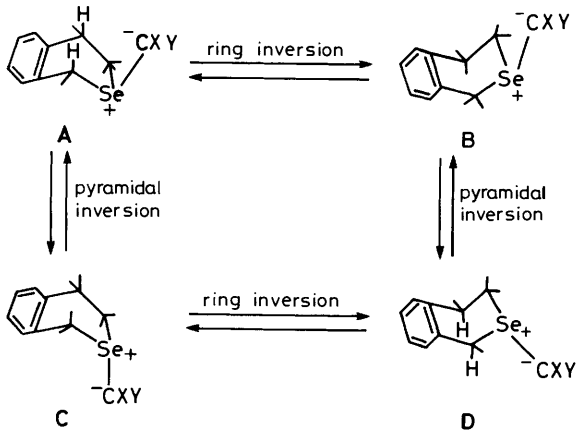
The ^{1}H n.m.r. spectra of all the ylides (**5a—e**) showed AB quartets assigned to 1-H, the methanide entities occupying the sterically relaxed pseudo-equatorial positions. In these configurations (**A** or **D** in Scheme 2), protons *cis* to the 1- and 4-positions of the methanide groups appear to lower magnetic fields as a result of the anisotropic effects of the methanide entities. The i.r. spectra of the compounds exhibited strong absorption, shifted *ca.* 100 cm^{-1} to lower frequency than the usual absorption for carbonyl and cyano groups. The effect indicates that the ylidic carbanions are delocalized over the electron-withdrawing groups. The spectral data are summarized in Table 2.



Scheme 1.

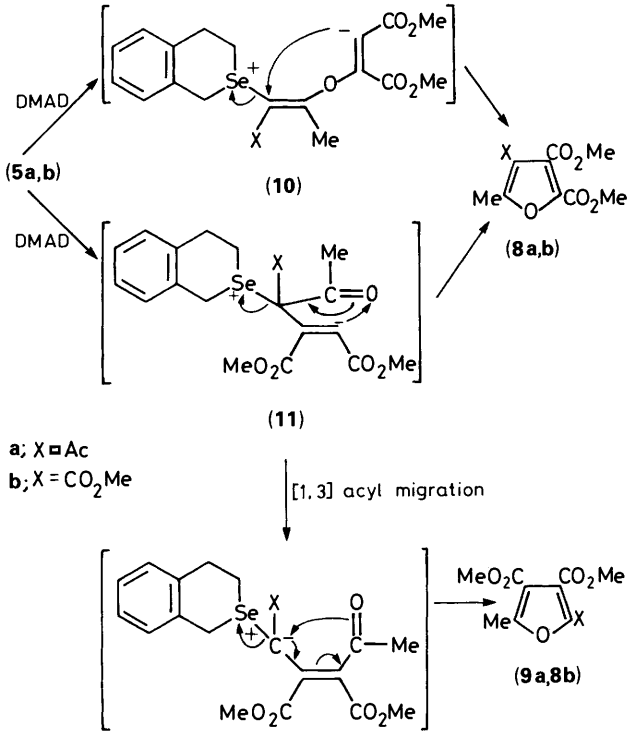
Reagents: i, 47% HBr aq., $CtPBu_3Br$; ii, $NaBH_4$, Se; iii, SO_2Cl_2, −30 °C; iv, 2 equiv. CH_2XY, MeONa; v, $NaClNTs{\cdot}3H_2O$; vi, 5 equiv. CH_2XY

Selenonium ylides (**5a—d**) were prepared using Method A in

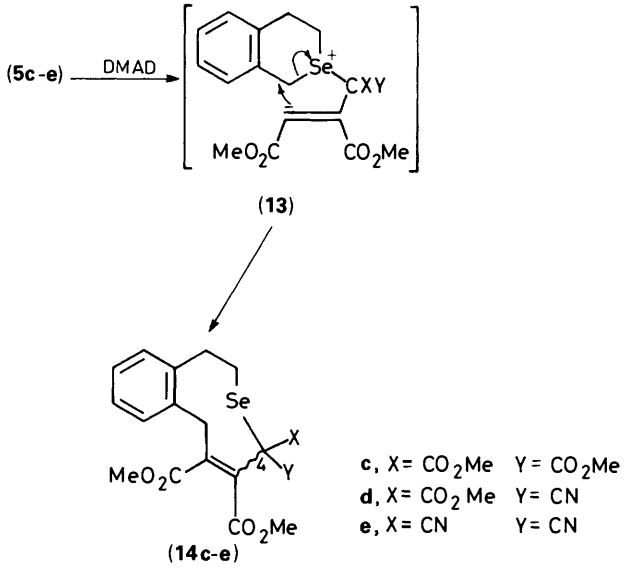


Scheme 2.

(7)



Scheme 3.



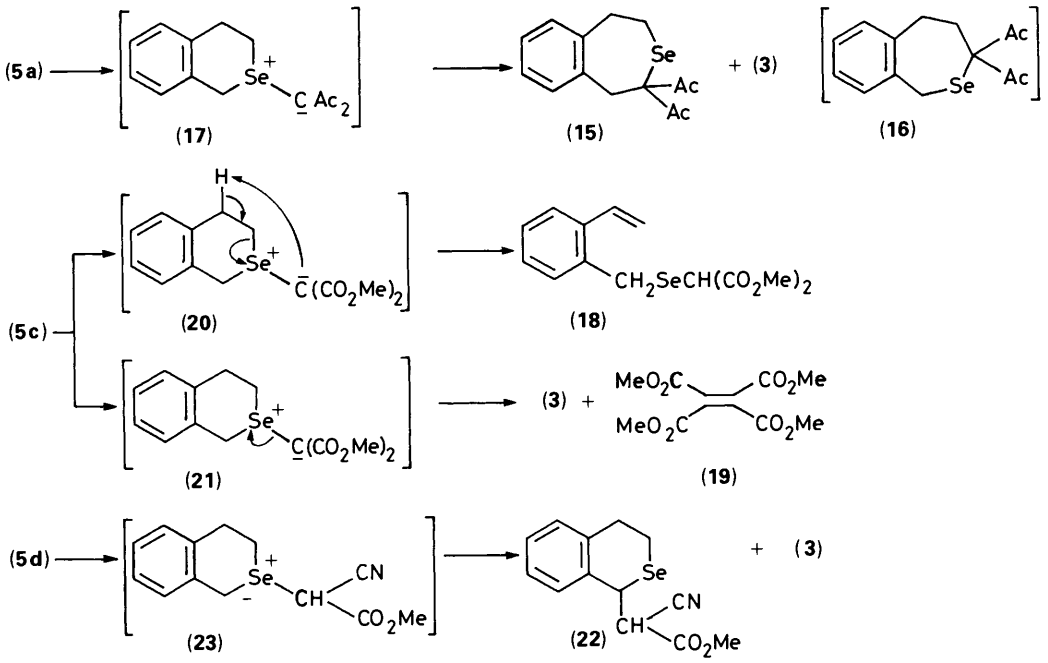
Scheme 4.

good yields. Method B was much better than Method A for the preparation of the dicyanomethanide (**5e**). Methanides stabilized by one electron-withdrawing group could not be obtained by the Methods A and B.

Treatment of the diacetylmethanide (**5a**) with fluoroboric acid gave the deacetylated product (**7**) in 82% yield. Its ^{1}H n.m.r. spectrum showed two kinds of double doublets at δ 3.86 and 4.28 assigned to the methylene protons of the acetonyl group and 1-H, respectively. The *exo*-C–Se bond is situated in a sterically less hindered pseudo-equatorial position and the proton 1-H *cis* to the methanide group appears at lower magnetic field. The geminal coupling of the acetonyl group is attributable to the proximity of the latter to the chiral centre of selenium. The other ylides (**5b**—**e**) when treated with fluoroboric acid, failed to give a product similar to (**7**) affording instead unidentified decomposition products. Magdesieva *et al.* reported a similar deacetylation with hydrochloric acid of a selenonium ylide stabilized by benzoyl and trifluoroacetyl groups.[4b]

Reactions of the Ylides (**5**) *with Dimethyl Acetylenedicarboxylate* (*DMAD*).—The diacetylmethanide (**5a**) reacted with DMAD to give two kinds of tetrasubstituted furans (**8a**) (51%) and (**9a**) (31%), and dihydro-1*H*-2-benzoselenin (**3**) (48%), while acetyl(methoxycarbonyl)methanide (**5b**) afforded a furan derivative (**8b**) (84%) and (**3**) (40%). A plausible mechanism for the formation of the furans (**8**) and (**9**) is shown in Scheme 3 by reference to that for (dimethylsulphonio)diacetylmethanide and DMAD;[9] compound (**8**) is formed *via* a betaine intermediate (**11**) produced by Michael addition of the ylide carbanion to DMAD, or *via* another betaine intermediate (**10**) produced by the addition of the enolate oxygen of the ylide to DMAD. On the other hand, the betaine intermediate (**11**) undergoes a [1,3] acyl migration to form an ylide intermediate (**12**). The ylide carbanion of (**12**) is enolised and the resulting enolate oxygen attacks nucleophilically at the carbon adjacent to the selenium to form the furan (**9**). No 1:2 adducts of (**5**):DMAD could be obtained. In the case of (**5b**), the methoxycarbonyl group did not participate in the formation of a furan derivative.

The other ylides (**5c**—**e**) having no acyl group(s) reacted with DMAD in a different manner to give ring-expanded benzoselenonine derivatives (**14c**—**e**) without furan derivatives (Scheme 4). The structures of (**14**) were established by ^{1}H n.m.r. and mass spectroscopy. Their mass spectra showed molecular ion peaks corresponding to 1:1 adducts. Their ^{1}H n.m.r. spectra showed 1-H signals at δ *ca.* 4.3, 0.7 p.p.m. to lower-field than that of (**3**), as a result of anisotropic effects of the electron-withdrawing groups. Furthermore, the ^{13}C n.m.r. spectrum of (**14d**) showed C-4 at δ 56 as a singlet. Although the products consisted of a single isomer, the *E,Z*-configuration of the double bond could not be determined, even though, from studies of Dreiding models, the *Z*-forms seem to be sterically less-hindered than the *E*-forms.



Scheme 5.

Table 1. Reactions of the ylides (**5c—e**) with DMAD

Compd.	Product (% yield)[a]
(**5c**)	(**14c**) (69), (**3**) (trace)[b]
(**5d**)	(**14d**) (79), (**3**) (trace)
(**5e**)	(**14e**) (24), (**3**) (10)

[a] Isolated yields. [b] Trace < 2%.

Formation of the benzoselenonine (**14**) begins with the Michael addition to DMAD to form a betaine intermediate (**13**), the vinylic carbanion of which nucleophilically attacks the benzylic carbon; this is followed by cleavage of the C–Se bond to form (**14**). Yields of the benzoselenonines (**14c—e**) are shown in Table 1. The low yield of (**14e**) may be ascribabed to the low solubility of (**5e**) in acetonitrile, the thermal decomposition then proceeding faster than the reaction with DMAD. The products of thermal decomposition were unidentified since their insolubility in most organic solvents precluded measurement of their n.m.r. spectra.

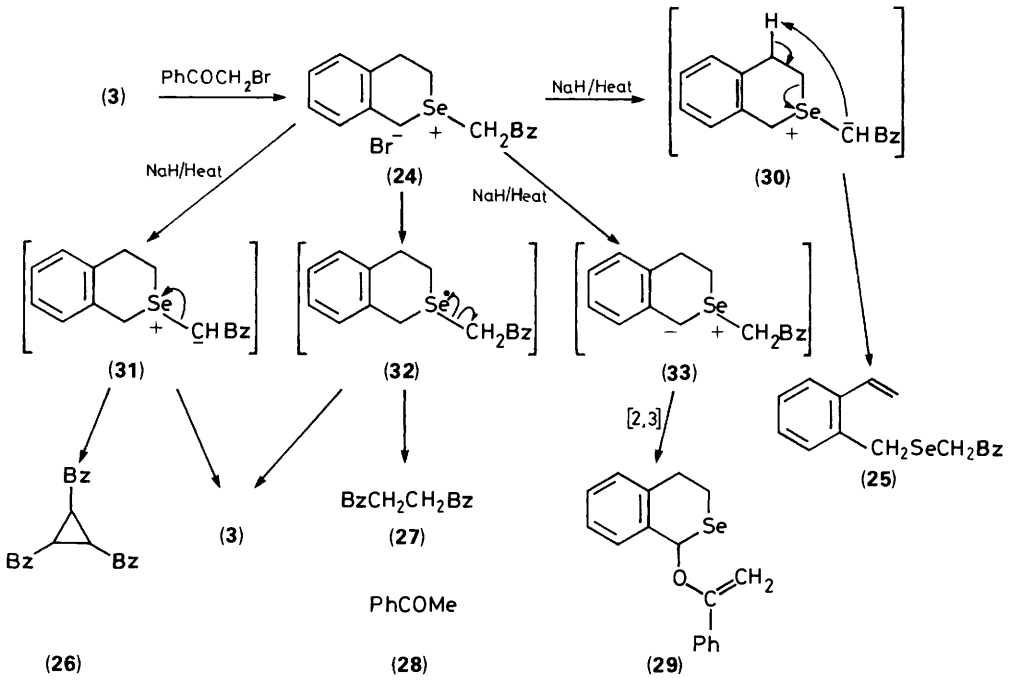
From these experiments, the enolate forms of the acetyl group in the ylides (**5a,b**) and the intermediate (**12**) played an important role in the formation of the furan derivatives (**8**) and (**9**), while the vinylic carbanion of the intermediates (**13**) produced from the ylides (**5c—e**) contributes to formation of the benzoselenonines (**14**).

Thermal Reactions of the Ylide (**5**).—Next, the thermal reactions of the ylides (**5**) were examined (see Scheme 5). Diacetylmethanide (**5a**) was refluxed in xylene to give the ring-expanded product 2,2-diacetyl-1,2,4,5-tetrahydro-3-benzoselenepine (**15**) (28%) and 3,4-dihydro-2-benzoselenin (**3**) (28%). Since the ^{1}H n.m.r. spectrum of the ring-expanded product showed signals for 1-H at δ 3.44, shifted 0.16 p.p.m. to higher field than 1-H for (**3**), it was impossible, on the basis of this evidence, to distinguish between structures (**15**) and (**16**) for the product. The ^{13}C 2D-INADEQUATE spectrum of the product showed two couplings between C-1 (δ 69.5) and C-2 (δ 36.3), and between C-4 (δ 20.5) and C-5 (δ 33.0). On the basis of this evidence therefore, the structure of the product was assigned as (**15**). When dimethoxycarbonylmethanide (**5c**) was heated in xylene, 2-[(dimethoxycarbonylmethyl)selenomethyl]styrene (**18**) (72%), tetramethyl ethylenetetracarboxylate (**19**) (17%), and (**3**) (12%) were obtained. On the other hand, thermolysis of cyano(methoxycarbonyl)methanide (**5d**) in xylene afforded the [1,2] rearranged product, methyl 1-cyano-1-(3,4-dihydro-2-benzoselenin-1-yl)acetate (**22**) (37%) and (**3**) (41%). Acetyl(methoxycarbonyl)methanide (**5b**) and the dicyanomethanide (**5e**) were thermally decomposed to (**3**) in 16% and 60% yields, respectively, and the other products were obtained as unidentified complex mixtures. The ^{1}H n.m.r. spectrum of the reaction mixture of (**5b**) indicated the presence of a styrene derivative but it could not be isolated.

Compound (**15**) is formed by a Stevens type [1,2] rearrangement of (**5a**). A similar mechanism was proposed for the ring expansion of the stable sulphonium ylides by Benati *et al.*[10] With (**5c**) and (**5d**), the ylide carbanion of each is deprotonated from the 1- or 4-position, the resulting intermediates (**20**) and (**23**) then undergoing either β-elimination or [1,2] rearrangement to form the styrene derivative (**18**) or the cyanoacetate (**22**), respectively. These reactions suggest that the ylide carbanions undergo attack either in configuration **A** or **D** (see Scheme 2). Although the nature of the product depends on the character of the ylide carbanion, its nucleophilicity, and its Brönsted basicity, it is unclear which is the controlling factor. Interestingly, while thermal reaction of the sulphur analogue of (**5c**), failed to give a ring-opened product it did afford a [1,2] rearranged product.[11]

However, the ethylene derivative (**19**) would be expected by dimerisation of the dimethoxycarbonylcarbene generated by decomposition of (**5c**). In the case of the other ylides (**5a**), (**5c—e**), the dihydro-1*H*-2-benzoselenin (**3**) was formed and therefore the disubstituted carbenes must be generated. However, these carbenes or their dimerised olefins would be very reactive and further reaction would proceed under the thermolysis conditions.

Synthesis and Reactions of (3,4-*Dihydro*-2-*benzoselenin*-2-*io*)*phenacylide* (**31**).—Since the title compound was not obtained



Scheme 6.

by the Methods A and B (Scheme 1), a synthesis by way of the selenonium salt was attempted. 2-Phenacyl-3,4-dihydro-2-benzoseleninium bromide (**24**) was prepared from (**3**) and phenacyl bromide (41%). Deprotonation of (**24**) with triethylamine, sodium hydride, and sodium alkoxides gave the unstable phenacylide (**31**) which could not be isolated.

The ylide (**31**), generated *in situ* from (**24**) and an equimolar amount of sodium hydride, was heated in benzene for 2 h to give the benzoselenin (**3**) (58%), 2-(phenacylselenomethyl)styrene (**25**), (24%), tribenzoylcyclopropane (26) (35%), 1,2-dibenzoylethane (**27**) (7%), acetophenone (**28**) (4%), and 1-(methylenebenzyloxy)-3,4-dihydro-2-benzoselenin (**29**) (3%). Cleavage of the *exo*-C–Se bond could occur two ways in the reaction: one, carbene formation followed by trimerisation to form the cyclopropane (**26**), and the other, radical cleavage by single-electron transfer from sodium hydride to the selenonium salt (**24**). The selenonium radical bearing nine electrons on the selenium atom would then collapse to form (**3**) and the phenacyl radical. Dimerisation of the radical or hydrogen abstraction from the solvent forms 1,2-dibenzoylethane (**27**) or acetophenone (**28**), respectively. We have already found that selenonium salts are easily reduced by metallic reagents *via* a single-electron transfer mechanism.[12] The unstable betaine (**30**), generated by abstraction 4-H by the ylide carbanion of (**31**) or directly by the base, decomposes to the styrene derivative (**25**). Compound (**29**) is formed by a [2,3] sigmatropic rearrangement of the unstable ylide (**33**) generated directly from (**24**) and sodium hydride or by isomerisation of (**31**). A similar [2,3] sigmatropic rearrangement is well known in the thermal reaction of some sulphonium phenacylides in the same solvent.[13] Our finding is the first example of a carbonyl group-participating rearrangement of a selenonium phenacylide.

Experimental

M.p.s were determined on a Yanagimoto micro melting point apparatus and are uncorrected. I.r. spectra of solids (KBr) and liquids (film) were recorded on a JASCO IRA-100 spectrophotometer. ^{1}H N.m.r. spectra were obtained for solutions in $CDCl_3$ on a Hitachi R-20B (60 MHz) or a JEOL GX-270 (270 MHz) spectrometer with tetramethylsilane as an internal standard, unless otherwise indicated. ^{13}C Spectra and a 2D INADEQUATE spectrum 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 were obtained on the JMA 2000 on-line system.

2-(2-*Bromoethyl*)*benzyl Bromide* (**2**).—A mixture of the benzopyran (**1**)[14] (10 g, 0.075 mol), 47% aqueous hydrobromic acid (127 ml), and tributyl(cetyl)phosphonium bromide (3.8 g) were heated at 115 °C for 5 h. The mixture was poured into water, and then extracted with dichloromethane. The dichloromethane layer was washed with water, dried ($MgSO_4$) and evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using hexane–dichloromethane (5:1) to give (**2**) (14.3 g, 70%) as pale yellow oil, δ_H 3.25–3.90 (4 H, m, 3-H, 4-H), 4.55 (2 H, s, 1-H) and 7.13—7.75 (4 H, m, ArH) (Found: M^+, 275.9168. $C_9H_{10}Br_2$ requires M, 275.9151).

Dihydro-2-benzoselenin (**3**).—Sodium borohydride (2.0 g, 53 mmol) was added to a suspension of selenium powder (2.8 g, 36 mmol) in ethanol (75 ml) to give a vigorous reaction and formation of sodium selenide as a pale yellow solution. The dibromide (**2**) (10 g, 36 mmol) was added to the latter solution in one portion and the mixture was refluxed for 2 h. It was then diluted with water (100 ml) and air passed through it for 5 h. After this the mixture was extracted with ether. The extracts were washed with water, dried ($MgSO_4$), and evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using hexane–dichloromethane (5:1) to give (**3**) (5.0 g, 70%) as colourless prisms, m.p. 44 °C (lit.,[6] 45—46 °C); δ_H 2.70—3.25 (4 H, m, 3-H, 4-H), 3.60 (2 H, s, 1-H), and 7.15 (4 H, br s, ArH); m/z 198 (M^+, Se = 80).

3,4-*Dihydro*-1H-2-*benzoselenin* 2,2-*Dichloride* (**4**).—Sulphuryl chloride (2.05 g, 15 mmol) was added to a solution of (**3**) (1.0 g, 15 mmol) in dry ether (60 ml) at −30 °C and the

Table 2. Spectral data of (3,4-dihydro-1*H*-2-benzoselenin-2-io)methanides (**5a—e**)

Compd.	1-H (*cis*)	1-H (*trans*)	δ_H ($CDCl_3$) (*J*/Hz, 3-H)	4-H	Others	$\nu_{max.}$/cm^{-1}	*m/z* (M^+)[a]
(**5a**)	5.01 (11)	3.98 (11)	2.94—3.50	3.50—3.89	2.44 (Me × 2) 7.25—7.30 (ArH)	1 550 (CO)	296
(**5b**)	5.14 (11)	3.92 (11)	2.95—3.33	3.53—3.88	2.48 (Me) 3.70 (OMe) 7.25—7.34 (ArH)	1 550 (CO) 1 660 (ester)	312
(**5c**)	5.05 (11)	3.99 (11)	3.03—3.31	3.55—3.85	3.74 (OMe × 2) 7.25—7.34 (ArH)	1 670 (ester)	328
(**5d**)	4.49 (12)	4.33 (12)	3.28—3.54	3.56—3.85	3.71 (Me) 7.27—7.38 (ArH)	1 630 (ester) 2 160 (CN)	295
(**5e**)[b]	4.43 (12)	4.23 (12)	3.18—3.28 3.70—3.79	3.18—3.28	7.27—7.52 (ArH)	2 140, 2 180 (CN)	262

[a] Se = 80. [b] Solvent was CD_3CN.

mixture was stirred for 2 h. A colourless precipitate formed and the temperature was gradually raised to ambient. The precipitate was filtered off, washed with dry ether, and dried *in vacuo* to give (**4**) (3.8 g, 94%) as colourless powder, m.p. 119—120 °C (decomp.); δ_H 3.55—4.10 (4 H, m, 3-H, 4-H), 4.90 (2 H, s, 1-H), and 7.20—7.55 (4 H, m, ArH); *m/z* 268 (M^+, Se = 80) (Found: C, 40.1; H, 3.6. $C_9H_{10}Cl_2Se$ requires C, 40.3; H, 3.8%). Since this compound was unstable at room temperature it was stored in a freezer.

General Procedure for (3,4-*Dihydro*-1H-2-*benzoselenin*-2-*io*)*methanides* (**5a—e**) *from* 3,4-*Dihydro*-2-*benzoselenin* 2,2-*Dichloride* (**4**) *and Enolates of Active Methylene Compounds* (*Method A*).—An active methylene compound (7.4 mmol) was added to a solution of sodium methoxide (7.4 mmol) in methanol (20 ml) and the mixture was stirred for 1 h at room temperature. It was then added to a suspension of (**4**) (1.0 g, 3.7 mmol) in methanol (20 ml). The mixture was stirred at room temperature for 3 h after which most of the solvent was removed under reduced pressure. The residual solid was dissolved in dichloromethane, and the solution washed with water, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was recrystallised from dichloromethane–ether. Spectral data are listed in Table 2. (3,4-*Dihydro*-1H-2-*benzoselenin*-2-*io*)*diacetylmethanide* (**5a**) (76%), colourless prisms from dichloromethane–hexane, m.p. 128 °C (decomp.) (Found: C, 56.8; H, 5.4. $C_{14}H_{16}O_2Se$ requires C, 56.95; H, 5.5%). (3,4-*Dihydro*-1H-2-*benzoselenin*-2-*io*)*acetyl*[*methoxycarbonyl*)*methanide* (**5b**) (72%), colourless prisms from dichloromethane–hexane, m.p. 102-105 °C (decomp.) (Found: C, 54.0; H, 5.2. $C_{14}H_{16}O_3Se$ requires C, 54.0; H, 5.2%). (3,4-*Dihydro*-1H-*benzoselenin*-2-*io*)*dimethoxycarbonylmethanide* (**5c**) (76%), colourless prisms from dichloromethane–hexane, m.p. 142–144 °C (decomp.) (Found: C, 51.1; H, 4.9. $C_{14}H_{16}O_4Se$ requires C, 51.4; H, 4.95%). (3,4-*Dihydro*-1H-*benzoselenin*-2-*io*)*cyano*(*methoxycarbonyl*)*methanide* (**5d**) (54%), pale yellow prisms from dichloromethane–hexane, m.p. 125—126 °C (decomp.) (Found: C, 52.8; H, 4.5; N, 4.85. $C_{13}H_{13}NO_2Se$ requires C, 53.1; H, 4.45; N, 4.8%) (3,4-*Dihydro*-1H-2-*benzoselenin*-2-*io*)*dicyanomethanide* (**5e**) (28%), colourless prisms, m.p. 96—98 °C (decomp.) (Found: C, 54.75; H, 3.9; N, 10.6. $C_{12}H_{10}N_2Se$ requires C, 55.2; H, 3.9; N, 10.6%). This sample (**5e**) was very unstable and all the physical measurements were recorded for unrecrystallised material; a high resolution mass spectrum could not be measured.

N-(3,4-*Dihydro*-1H-2-*benzoselenin*-2-*io*)*toluene*-p-*sulphonamidate* (**6**).—Chloramine T trihydrate (1.43 g, 5 mmol) was added to a solution of (**3**) (1.0 g, 5 mmol) in a mixture of dichloromethane (30 ml) and acetonitrile (30 ml), and the resulting mixture was stirred for 12 h at room temperature. Most of the solvent was then removed under reduced pressure and the residual solid was dissolved in dichloromethane, and the solution washed with water, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was recrystallised from dichloromethane–ether to give (**6**) (1.27 g, 68%) as colourless powder, m.p. 125—126 °C (decomp.); δ_H 2.39 (3 H, s, Me), 3.00—3.60 (4 H, m, 3-H, 4-H), 3.95 (1 H, d, *J* 12 Hz, 1-H), 4.60 (1 H, d, *J* 12 Hz, 1-H), 7.15—7.55 (6 H, m, ArH), and 7.70—8.05 (2 H, m, ArH); $\nu_{max.}$ 1 255 and 970 cm^{-1} (SO_2) (Found: M^+, 367.0119. $C_{16}H_{17}NO_2SSe$ requires *M*, 367.0144).

General Procedure for (3,4-*Dihydro*-1H-*benzoselenin*-2-*io*)*methanides* (**5a—e**) *from the Sulphonamidate* (**6**) *and Active Methylene Compounds* (*Method B*).—An active methylene compound (5 mol equiv.) was added to a solution of (**6**) (300 mg, 0.8 mmol) in dry chloroform (15 ml) and the mixture was stirred overnight. The solvent was then removed under reduced pressure and the residual solid was washed with ether and recrystallised from dichloromethane–ether to give an ylide: (**5a**) (33%), (**5b**) (38%), (**5c**) (9%), (**5d**) (42%), or (**5e**) (94%). Each product was identical (^{1}H n.m.r. and i.r.) with an authentic specimen prepared by method A.

Reaction of the Diacetylmethanide (**5a**) *with Fluoroboric Acid.*—42% Fluoroboric acid (146 mg, 0.7 mmol) was added to a solution of (**5a**) (100 mg, 0.34 mmol) in methanol (5 ml) at 0 °C and the mixture was stirred overnight. After this it was dried ($MgSO_4$), evaporated under reduced pressure, and the residue was recrystallised from methanol–ether to give 2-*acetonyl*-3,4-*dihydro*-1H-*benzoselenin*-2-*ium tetrafluoroborate* (**7**) (95 mg, 82%) as colourless prisms, m.p. 118—120 °C; δ_H(CD_3CN) 2.18 (3 H, s, Me), 2.90—3.12 (2 H, m, 3-H), 3.29—3.38 (1 H, m, 4-H), 3.69—3.76 (1 H, m, 4-H), 3.86 (2 H, dd, *J* 20, 17 Hz, $COCH_2$), 4.28 (2 H, dd, *J* 19, 13 Hz, $SeCH_2Ar$), and 7.38—7.56 (4 H, m, ArH); $\nu_{max.}$ 1 715 (CO) and 1 095 cm^{-1} (BF_4) (Found: C, 42.0; H, 4.4. $C_{12}H_{15}BF_4OSe$ requires C, 42.3; H, 4.4%).

General Procedure for the Reaction of the Ylides (**5a—e**) *with Dimethyl Acetylenedicarboxylate* (*DMAD*).—DMAD (2 mol equiv.) was added to a solution of (**5a—e**) (300 mg) in dry acetonitrile (10 ml) and the mixture was refluxed for 8 h under nitrogen. It was then evaporated under reduced pressure and the residue was separated by preparative t.l.c. on silica gel using hexane–ethyl acetate (5:1). *Dimethyl* 3-*acetyl*-5-*methylfuran*-4,5-*dicarboxylate* (**8a**) (124 mg, 51%), colourless prisms from dichloromethane–hexane, m.p. 59—61 °C; δ_H 2.46 (3 H, s, Me), 2.68 (3 H, s, Me), 3.88, and 3.99 (3 H × 2, s, OMe × 2); $\nu_{max.}$ 1 750, 1 730, 1 255, 1 230 (ester), 1 680 (CO), 1 600, 1 400, and 860 cm^{-1} (furan); *m/z* 240 (M^+) (Found: C, 54.7; H, 5.0. $C_{11}H_{12}O_6$ requires C, 55.0; H, 5.0%). *Dimethyl* 2-*acetyl*-5-

methylfuran-3,4-*dicarboxylate* (**9a**) (92 mg, 38%), colourless prisms from dichloromethane–hexane, m.p. 79—81 °C; δ_H 2.40 (3 H, s, Me), 2.70 (3 H, s, Me), 3.92, and 3.99 (3 H × 2, s, OMe × 2); $\nu_{max.}$ 1 750, 1 730, 1 240, 1 200 (ester), 1 760 (CO), 1 600, 1 400, and 855 cm^{-1} (furan); *m/z* 240 (M^+) (Found: C, 54.7; H, 5.0. $C_{11}H_{12}O_6$ requires C, 55.0; H, 5.0%). *Trimethyl* 5-*methylfuran*-2,3,4-*tricarboxylate* (**8b**) (244 mg, 84%), colourless needles from dichloromethane–hexane, m.p. 97—99 °C; δ_H 2.65 (3 H, s, Me), 3.85, 3.90, and 3.95 (3 H × 3, s, Me × 3); $\nu_{max.}$ 1 760, 1 725, 1 270, 1 225 (ester), 1 610, 1 410, and 885 cm^{-1} (furan); *m/z* 256 (M^+) (Found: C, 51.3; H, 4.7. $C_{11}H_{12}O_7$ requires C, 51.6; H, 4.7%). *Tetramethyl* 1,2,4,7-*tetrahydro*-3-*benzoselenonine*-4,4,5,6-*tetracarboxylate* (**14c**) (297 mg, 69%), yellow oil, δ_H 2.80—3.10 (2 H, m, 4-H), 3.20—3.45 (2 H, m, 5-H), 3.55, 3.63, 3.78, 3.83 (3 H × 4, s, Me × 4), 4.30 (2 H, s, 1-H), and 7.00—7.80 (4 H, m, ArH); $\nu_{max.}$ 1 765, 1 740, 1 730, 1 270, 1 260, and 1 240 cm^{-1} (Found: M^+, 470.0411. $C_{20}H_{22}O_8Se$ requires *M*, 470.0478). *Trimethyl* 4-*cyano*-1,2,4,7-*tetrahydro*-3-*benzoselenonine*-4,5,6-*tricarboxylate* (**14d**) (351 mg, 79%), yellow amorphous solid, δ_H 2.92—3.32 (2 H, m, 4-H), 3.64—3.69 (2 H, m, H-5), 3.75, 3.76, 3.88 (3 H × 3, s, Me × 3), 4.07 (1 H, dd, *J* 12, *ca.* 0 Hz, 1-H), and 7.07—7.55 (4 H, m, ArH); δ_C 22.5 (t), 32.7 (t), 39.4 (t), 52.7 (q), 52.9 (q), 54.7 (q), 116.5 (s), 126.4 (s), 127.1 (d), 128.3 (d), 129.7 (d), 131.4 (d), 134.5 (s), 139.6 (s), 141.9 (s), 164.2 (s), and 166.6 (s); $\nu_{max.}$ 2 240 (CN), 1 770 and 1 255 cm^{-1} (ester) (Found: M^+, 437.0361. $C_{19}H_{19}NO_6Se$ requires *M*, 437.0376). *Dimethyl* 4,4-*dicyano*-1,2,4,7-*tetrahydro*-3-*benzoselenonine*-5,6-*dicarboxylate* (**14e**) (112 mg, 24%), colourless prisms from dichloromethane–hexane, m.p. 182—184 °C; δ_H 3.10—3.45 (4 H, m, 4-H, 5-H), 3.75, 3.81 (3 H × 2, s, Me × 2), 4.30 (2 H, s, 1-H), and 7.22—7.75 (4 H, m, ArH); $\nu_{max.}$ 2 220 (CN), 1 730, and 1 265 cm^{-1} (ester); *m/z* 404 (M^+, Se = 80) (Found: C, 53.4; H, 4.0; N, 7.0. $C_{18}H_{16}N_2O_4Se$ requires C, 53.6; H, 4.0; N, 6.95%).

Thermal Reaction of Diacetylmethanide (**5a**).—A suspension of (**5a**) (300 mg, 1.0 mmol) in xylene (15 ml) was refluxed under nitrogen for 2 h. After this the solvent was removed under reduced pressure and the residue was separated by preparative t.l.c. on silica gel using hexane–dichloromethane (3:2) to give (**3**) (55 mg, 28%) and 2,2-*diacetyl*-1,2,4,5-*tetrahydro*-3-*benzoselenepine* (**15**) (165 mg, 56%) as colourless prisms from dichloromethane–hexane, m.p. 126—127 °C; δ_H 2.28 (6 H, s, Me × 2), 2.92 (2 H, t, *J* 6.3 Hz, 4-H), 3.21 (2 H, t, *J* 6.3 Hz, 5-H), 3.44 (2 H, s, 1-H), and 6.93—7.26 (4 H, m, ArH); δ_C 20.5 (t), 27.8 (q), 33.0 (t), 36.3 (t), 69.5 (s), 126.8 (d), 127.6 (d), 129.6 (d), 130.0 (d), 135.7 (s), 139.3 (s), and 201.3 (s); $\nu_{max.}$ 1 675 cm^{-1} (CO); *m/z* 296 (M^+, Se = 80) (Found: C, 56.8; H, 5.5 $C_{14}H_{16}O_2Se$ requires C, 56.95; H, 5.5%).

Thermal Reaction of the Dimethoxycarbonylmethanide (**5c**).—A suspension of (**5c**) (300 mg, 1.0 mmol) in xylene (15 ml) was refluxed under nitrogen for 2 h. The solvent was removed under reduced pressure and the residue was separated by preparative t.l.c. on silica gel using hexane–dichloromethane (3:2) to give (**3**) (22 mg, 12%), 2-[(*dimethoxycarbonylmethyl*)*selenomethyl*]-*styrene* (**18**) (215 mg, 72%) as a yellow oil; δ_H 3.63 (1 H, s, CH), 3.79 (6 H, s Me × 2), 4.20 (2 H, s, CH_2), 5.39 (1 H, dd, *J* 10.5, 1.2 Hz, $=CH_2$), 5.70 (1 H, dd, *J* 17.3, 1.2 Hz, $=CH_2$), 7.10 (1 H, dd, *J* 17.3, 10.5 Hz, =CH), and 7.20—7.50 (4 H, m, ArH); $\nu_{max.}$ 1 750 cm^{-1} (Found: M^+, 328.0199. $C_{14}H_{16}O_4Se$ requires *M*, 328.0213), and tetramethyl ethylenetetracarboxylate (**19**) (20 mg, 17%) as colourless prisms from dichloromethane–hexane, m.p. 118—119 °C (lit.,[15] 119—120 °C); δ_H 3.80 (12 H, s, Me × 4); *m/z* 260 (M^+).

Thermal Reaction of Cyano(*methoxycarbonyl*)*methanide* (**5d**).—A suspension of (**5d**) (300 mg, 1.0 mmol) in xylene (15 ml) was refluxed under nitrogen for 2 h. The solvent was removed under reduced pressure and the residue was separated by preparative t.l.c. on silica gel using hexane–ethyl acetate (5:1) to give (**3**) (84 mg, 41%) and *methyl* 1-*cyano*-1-(3,4-*dihydro*-1H-2-*benzoselenin*-1-*yl*)*acetate* (**22**) (110 mg, 37%) as a yellow oil, δ_H 3.14—3.53 (4 H, m, 3-H, 4-H), 3.37 (1 H, d, *J* 6.0 Hz, CH), 3.83 (1 H, d, *J* 6.0 Hz, 1-H), 3.89 (3 H, s, Me), and 7.13—7.29 (4 H, m, ArH); $\nu_{max.}$ 2 240 (CN) and 1 740 cm^{-1} (ester) (Found: M^+, 295.0125. $C_{13}H_{13}NO_2Se$ requires *M*, 295.0111).

2-*Phenacyl*-3,4-*dihydro*-1H-2-*benzoseleninium Bromide* (**24**).—Phenacyl bromide (300 mg, 1.5 mmol) was added to a warm solution of (**3**) (300 mg, 1.5 mmol) in ethanol (5 ml) and the mixture was refluxed for 5 min. The solvent was then removed under reduced pressure and the residue was recrystallised from benzene–ether to give (**24**) (246 mg, 41%) as colourless powder, m.p. 107 °C; $\delta_H(CD_3CN)$ 2.83—2.87 (2 H, m, 3-H), 2.97—3.01 (2 H, m, 4-H), 3.68 (2 H, s, $COCH_2$), 4.56 (2 H, s, $SeCH_2Ar$), and 7.21—8.00 (20 H, m, ArH); $\nu_{max.}$ 1 660 cm^{-1} (CO) (Found: C, 51.45; H, 4.4. $C_{17}H_{17}BrOSe$ requires C, 51.55; H, 4.3%).

Reaction of the Selenonium Salt (**24**) *with Sodium Hydride*.—The selenonium salt (**24**) (396 mg, 1.0 mmol) was added to a suspension of sodium hydride (24 mg, 1.0 mmol) in dry benzene (15 ml) and the mixture was stirred for 1 h under nitrogen; it was then refluxed for 2 h. The cooled mixture was washed with water, dried ($MgSO_4$) and evaporated under reduced pressure and the residue was separated by preparative t.l.c. on silica gel using hexane–dichloromethane (3:2) to give (**3**) (114 mg, 58%), *trans*-tribenzoylcyclopropane (**26**) (41 mg, 35%) as colourless prisms, 1,2-dibenzoylethane (**27**) (8 mg, 7%) as colourless prisms from dichloromethane–hexane, m.p. 143—144 °C, acetophenone (**28**) (5 mg, 4%) as a colourless oil, 2-(*phenacylselenomethyl*)*styrene* (**25**) (74 mg, 24%) as an oil, δ_H 3.76 (2 H, s, $ArCH_2$), 3.95 (2 H, s, $COCH_2$), 5.32 (1 H, dd, *J* 11.2, 1.4 Hz, $=CH_2$), 5.67 (1 H, dd, *J* 17.2, 1.4 Hz, $=CH_2$), 7.00 (1 H, dd, *J* 17.2 11.2 Hz, =CH), 7.17—7.33 (3 H, m, ArH), 7.44—7.60 (4 H, m, ArH), and 7.91—7.95 (2 H, m, ArH); $\nu_{max.}$ 1 667 (CO), 3 075, and 1 820 cm^{-1} (C=CH_2) (Found: M^+, 316.0379. $C_{17}H_{16}OSe$ requires *M*, 316.0367), and 1-(*methylenebenzyloxy*)-3,4-*dihydro*-1H-2-*benzoselenin* (**29**) (9 mg, 3%) as an oil, δ_H 3.17—3.22 (4 H, m, 3-H, 4-H), 4.82 (2 H, s, $=CH_2$), 5.93 (1 H, s, CH), and 7.02—7.50 (9 H, m, ArH) (Found: M^+, 316.0386. $C_{17}H_{16}OSe$ requires *M*, 316.0366). Compounds (**25**) and (**26**) were identical with authentic samples of (**25**)[16] and (**26**)[17].

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References

1 M. Hori, T. Kataoka, H. Shimizu, and K. Tsutsumi, *J. Org. Chem.*, 1987, **52**, 1397.
2 (*a*) K. Tanaka, J-I. Hayashi, and A. Kaji, *Phosphorus and Sulfur*, 1983, **16**, 201; (*b*) R. H. Fish, L. C. Chow, and M. C. Casserio, *Tetrahedron Lett.*, 1969, 1259; (*c*) C. Kissel, R. J. Holland, and M. C. Casserio, *J. Org. Chem.*, 1972, **37**, 2720.
3 (*a*) I. Hargittai and B. Rozsondai 'The Chemistry of Organic Selenium and Tellurium Compounds,' ed. S. Patai and Z. Rappoport, John Wiley and Sons, New York, 1986, ch. 3; (*b*) C. Paulmier, 'Selenium Reagents and Intermediates in Organic Synthesis,' ed. J. E. Baldwin, Pergamon Press, New York, 1986, p. 4.
4 (*a*) Ref. 3*b*, p. 162; (*b*) N. N. Magdesieva, *Russ. Chem. Rev.* (*Engl. Transl.*), 1988, **57**, 161.
5 B. M. Trost and L. S. Melvin, Jr., 'Sulfur Ylides,' Academic Press, New York, 1975.
6 F. G. Holliman and F. G. Mann, *J. Chem. Soc.*, 1945, 37.

7 (*a*) N. N. Magdesieva, R. A. Kyandzhetsian, and O. A. Rakitin, *J. Org. Chem. USSR* (*Engl. Transl.*), 1976, 33; (*b*) N. N. Magdesieva, R. A. Kandgetcyan, and A. A. Ibragimov, *J. Organometal. Chem.*, 1972, **42**, 399.
8 S. Tamagaki and K. Sakaki, *Chem. Lett.*, 1975, 503.
9 (*a*) Y. Hayasi, M. Kobayasi, and H. Nozaki, *Tetrahedron*, 1970, **26**, 4353; (*b*) M. Takaku, Y. Hayasi, and H. Nozaki, *Tetrahedron Lett.*, 1969, 2053; (*c*) M. Higo and T. Mukaiyama, *ibid.*, 1970, 2565.
10 L. Benati, P. C. Montevecchi, and P. Spagnolo, *J. Chem. Soc., Perkin Trans. 1*, 1982, 917.
11 R. Pellicciari, M. Curini, and P. Ceccherelli, *J. Chem. Soc., Chem. Commun.*, 1977, 1155.
12 M. Hori, T. Kataoka, H. Shimizu, and K. Tsutsumi, *Tetrahedron Lett.*, 1989, **30**, 981.
13 (*a*) T. Kataoka, A. Tomoto, H. Shimizu, and M. Hori, *J. Chem. Soc. Perkin Trans. 1*, 1984, 515; (*b*) A. Terada and Y. Kishida, *Chem. Pharm. Bull.*, 1970, **18**, 505; (*c*) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, 1968, **33**, 70.
14 A. Riehe and E. Shmitz, *Chem. Ber.*, 1956, **89**, 1254.
15 B. B. Corson, R. K. Hazen, and J. S. Thomas, *J. Am. Chem. Soc.*, 1928, **50**, 913.
16 B. M. Trost, *J. Am. Chem. Soc.*, 1967, **89**, 138.
17 C. Weygand and W. Meusel, *Chem. Ber.*, 1943, **76**, 498.

Received 4*th April* 1989; *Paper* 9/01362H