Conversion of Aldehydes and Ketones into Selenoacetals: Use of Tris(phenylseleno)borane and Tris(methylseleno)borane

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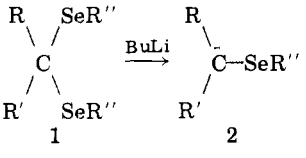
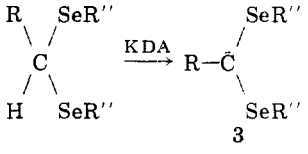
In the presence of trifluoroacetic acid, aldehydes and ketones react with tris(phenylseleno)borane and with tris(methylseleno)borane to give the corresponding bis(phenylseleno)- and bis(methylseleno)acetals, respectively. Suitable reaction periods lie in the approximate range 20 min–24 h and generally about 12 mol % (based on the carbonyl compound) of TFA is required. The borane reagents are not suitable for α,β-unsaturated carbonyl compounds, but, where the reagents are applicable, yields averaged 78%.

As a compound class, selenoacetals 1 have been known for many years,[1] and they have recently begun to be studied in detail. Substantial literature now exists[2-18] and the modern work has shown the compounds to have considerable promise in synthetic methodology on the basis of three characteristic properties. (A) Reaction with BuLi affords selenium-stabilized carbanions (eq 1). (B) Deprotonation with potassium diisopropylamide–lithium *tert*-butoxide (KDA) also gives carbanions (eq 2). (C) Reduction with triphenyltin hydride produces hydrocarbons (eq 3).



(1)

1 2



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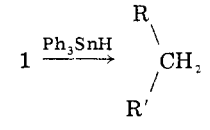
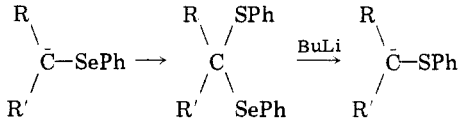


(3)

The carbanions of type 2 are particularly useful for making C–C bonds in a variety of environments[7-10,13a-g,14] and also as a route (eq 4) to other heteroatom-stabilized carbanions,[13h-j] some of which are not available[13i,j,15] by deprotonation.



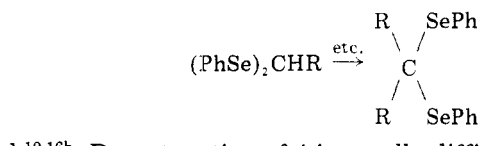
(4)

Species 3 also react with electrophiles,[13k,16] and the products can be converted into new selenium-stabilized carbanions by the method of eq 1.

The triphenyltin hydride reaction (eq 3) constitutes a method for reducing carbonyl groups in the sense $>C{=}O \rightarrow >CH_2$ and is applicable[17] to the formation of deuterated species.

A prerequisite to the use of selenoacetals is that they be easy to prepare by a variety of methods. The conventional route involves what seem to be drastic conditions because it calls for saturating a mixture of the carbonyl compound and a selenol with HCl gas.[6,7,10] Newer procedures involve the use of concentrated sulfuric acid (1 mol/mol of carbonyl compound)[6] or of zinc chloride (0.5 mol/mol of substrate).[6]

Acidic conditions can be avoided by the alkylation process of eq 5 and several examples of this type have been



(5)

reported.[10,16b] Deprotonation of 4 is usually difficult,[16b] but KDA[16b,19] may prove generally useful for this purpose.

Finally, there are specialized methods that involve the reaction of diazomethane with diphenyl diselenide[11] and the reaction of selenols with α-chloro ethers.[12]

(1) E.g.: Shaw, E. H.; Reid, E. E. *J. Am. Chem. Soc.* **1926**, *48*, 520. Loevenich, J.; Fremdling, H; Fröhr, M. *Chem. Ber.* **1929**, *62*, 2856. Early work is reviewed briefly by: Klayman, D. L. In "Organic Selenium Compounds: Their Chemistry and Biology"; Klayman, D. L., Günther, W. H. H., Eds.; Wiley-Interscience: New York, 1973; p 86.

(2) There is extensive overlap in coverage, but an approximate classification of the literature is that ref 4–12 contain pertinent data on synthesis of selenoacetals and ref 13–18 on their properties.

(3) Part of the chemistry of selenoacetals has been reviewed: Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22.

(4) Clive, D. L. J.; Menchen, S. M. *J. Chem. Soc., Chem. Commun.* **1978**, 356.

(5) Clive, D. L. J.; Menchen, S. M. *J. Org. Chem.* **1979**, *44*, 1883.

(6) Dumont, W.; Krief, A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 540.

(7) Van Ende, D.; Dumont, W.; Krief, A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 700.

(8) Sevrin, M.; Krief, A. *Tetrahedron Lett.* **1978**, 187.

(9) Halazy, S.; Lucchetti, J.; Krief, A. *Tetrahedron Lett.* **1978**, 3971.

(10) Seebach, D.; Peleties, N. *Chem. Ber.* **1972**, *105*, 511.

(11) Petragnani, N.; Schill, G. *Chem. Ber.* **1970**, *103*, 2271.

(12) Lapkin, I. I.; Pavlova, N. N.; Pavlov, G. S. *J. Org. Chem. USSR (Engl. Transl.)* **1970**, *6*, 71; *Zh. Org. Khim.* **1970**, *6*, 71.

(13) (a) Dumont, W.; Bayet, P.; Krief, A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 804. (b) Dumont, W.; Krief, A. *Ibid.* **1975**, *14*, 35. (c) *Ibid.* **1976**, *15*, 161. (d) Rémion, J.; Dumont, W.; Krief, A. *Tetrahedron Lett.* **1976**, 1385. (e) Denis, J. N.; Dumont, W.; Krief, A. *Ibid.* **1976**, 453. (f) Van Ende, D.; Krief, A. *Ibid.* **1976**, 457. (g) Labar, D.; Dumont, W.; Hevesi, L.; Krief, A. **1978**, 1145. (h) Anciaux, A.; Eman, A.; Dumont, W.; Van Ende, D.; Krief, A. *Ibid.* **1975**, 1613. (i) Anciaux, A.; Eman, A.; Dumont, W.; Krief, A. *Ibid.* **1975**, 1617. (j) Seebach, D.; Beck, A. K. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 806. (k) Van Ende, D.; Dumont, W.; Krief, A. *J. Organomet. Chem.* **1978**, *149*, C10.

(14) Cf.: Sevrin, M.; Dumont, W.; Krief, A. *Tetrahedron Lett.* **1977**, 3835.

(15) Seebach, D.; Meyer, N.; Beck, A. K. *Justus Liebigs Ann. Chem.* **1977**, 846.

(16) (a) Gröbel, B.-T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852. (b) Raucher, S.; Koolpe, G. A. *J. Org. Chem.* **1978**, *43*, 3794.

(17) (a) Clive, D. L. J.; Chittattu, G. J.; Wong, C. K. *J. Chem. Soc., Chem. Commun.* **1978**, 41. Bis(methylseleno)acetals can also be reduced (unpublished observations). (b) Sevrin, M.; Van Ende, D.; Krief, A. *Tetrahedron Lett.* **1976**, 2643.

(18) Lehn, J.-M.; Wipff, G.; Demuynck, J. *Helv. Chim. Acta* **1977**, *60*, 1239.

(19) See: Renger, B.; Hügel, H.; Wykypiel, W.; Seebach, D. *Chem. Ber.* 1978, *111*, 2630 for other uses of KDA.

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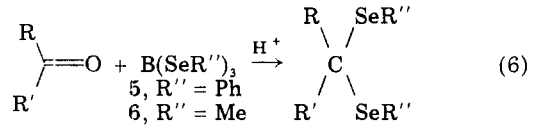
In the present work tris(phenylseleno)borane (**5**)[20] and tris(methylseleno)borane (**6**)[21] have been found to be useful reagents for making selenoacetals (eq 6). Both compounds



(6)

are readily accessible. The preparation of the former (eq 7) requires benzeneselenol, but this material does not have

$$BBr_3 + PhSeH \longrightarrow \underset{\mathbf{5}}{B(SePh)_3} \qquad (7)$$

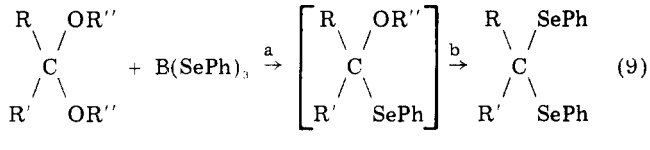
to be of high quality as any diphenyl diselenide present is removed during workup, and tris(phenylseleno)borane can be obtained in about 75% yield as off-white crystals. The methyl analogue, $B(SeMe)_3$, which is a liquid, is prepared (eq 8) from dimethyl diselenide, itself easy to make[22]

$$MeSeSeMe \xrightarrow[2.\ BF_3\cdot Et_2O]{1.\ LiAlH_4} \underset{\mathbf{6}}{B(SeMe)_3} \qquad (8)$$

and also commercially available.[23] Both borane reagents react with water, but the impression gained from working with them is that, in a dry atmosphere, they are less sensitive to oxygen than the parent selenols. It is convenient to store the working supply of $B(SeMe)_3$ in a syringe from which the compound can be dispensed as required. In order to maintain the quality of the stock of $B(SePh)_3$, repetitive exposure to air should be avoided, and the container is best manipulated inside a nitrogen-filled glovebag. Compared with pure selenols, the borane reagents not only are convenient carriers of the PhSe and MeSe groups but also allow the preparation of selenoacetals under conditions that are milder than those previously reported.[6]

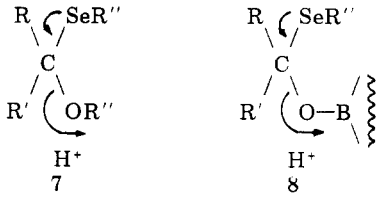
Apart from cases where the reagents are clearly not applicable (see Table I, preparation of compounds **23**, **24**, **26**, and **27**) the average yield for 14 other examples is 78%. Isolation of the bis(seleno)acetals is usually straightforward, and two procedures, besides chromatography and crystallization, are available for removing diselenides that are formed as byproducts: PhSeSePh can be converted into the water-soluble salt, $PhSe^-Na^+$, by the action of $NaBH_4$,[24] and, in principle, MeSeSeMe can be removed from nonvolatile acetals by evaporation.[25]

For the preparation of selenoacetals the presence of a small amount of acid is almost always required. Trifluoroacetic acid (TFA) is generally useful, but *p*-toluenesulfonic acid can sometimes be used (e.g., see preparation of **17** and **20**).[26] The amount of TFA needed is generally about 12 mol % on the basis of the carbonyl substrate. In a related process both reagents **5** and **6** react with acetals (eq 9).[5] Also, as expected, these borane reagents afford



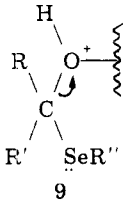
(9)

selenols when treated with TFA, but such a process is not involved in the first stage (a) of eq 9 as no acid is required.[5] The second stage (b) does need[5] acid whose function, probably, is to assist the expulsion of R″O (see **7**). The



amount of acid needed for fast reaction is sensitive to the reagent used.[27] In the case of aldehydes and ketones a comparable role for acid is summarized in **8**. The preparation of compounds **13** and **14** (see Table I) can be done without acid. Evidence is available to suggest that in cases where the presence of acid is a definite requirement, the reaction for carbonyl compounds, like that for acetals, also occurs in stages. For example, when undecanal is treated with $B(SeMe)_3$, the aldehyde proton disappears rapidly from the NMR spectrum,[28] but formation of the bis(methylseleno)acetal **21** is very slow. Addition of TFA results in rapid generation of **21**.

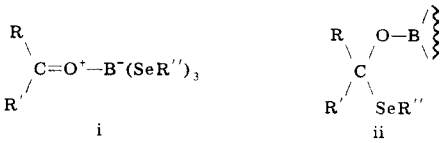
A number of factors, not all mutually assisting, are likely to be involved in the reaction of carbonyl compounds with the borane reagents. On the basis of the relative availability of a selenium lone pair in methyl and phenyl selenides,[7] $B(SeMe)_3$ is expected to be a weaker Lewis acid than $B(SePh)_3$. Also, process **9**[29] with R″ = Me should be easier



than **9** with R″ = Ph. If nucleophilic attack by MeSeH or PhSeH is involved, the former is predicted to be the easier.[27,30]

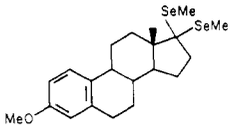
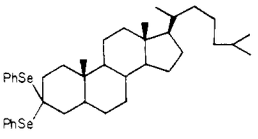
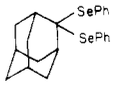
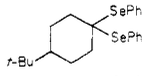
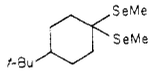
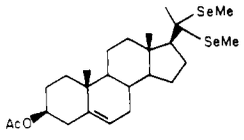
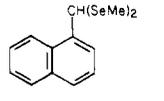
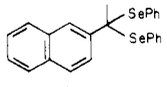
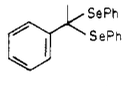
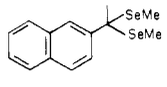
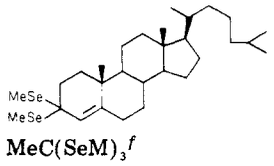
The results collected in Table I as well as some other observations suggest the following trends. (i) For cyclic C_5, cyclic C_6, and acyclic ketones the formation of bis(methylseleno)acetals is faster than the formation of bis(phenylseleno)acetals (cf. the formation of **10** and **11**, **15** and **16**, and **17** and **18**). (ii) For use with aryl alkyl ketones, $B(SeMe)_3$ appears to be a better reagent than $B(SePh)_3$

(20) Schmidt, M.; Block, H. D. *J. Organomet. Chem.* **1970**, *25*, 17.
(21) Siebert, W.; Ruf, W.; Full, R. *Z. Naturforsch. B* **1975**, *30*, 642.
(22) (a) Bird, M. L.; Challenger, F. *J. Chem. Soc.* **1942**, 570. (b) For another general route see: Klayman, D. L.; Griffin, T. S. *J. Am. Chem. Soc.* **1973**, *95*, 197.
(23) Available from Ventron Corp.
(24) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697.
(25) This technique has been used in another context: Clive, D. L. J.; Menchen, S. M. *J. Chem. Soc., Chem. Commun.* **1979**, 168.
(26) $BF_3\cdot Et_2O$ was evaluated as a catalyst (for the preparation of **19**) but was without effect. In the course of examining other Lewis acids, BBr_3 was found, on the basis of NMR measurements, to convert $C_{10}H_{21}CH(OMe)_2$ into $C_{10}H_{21}CHBr_2$. Cf.: Lansinger, J. M.; Ronald, R. C. *Synth. Commun.* **1979**, *9*, 341.
(27) Treatment of $C_{10}H_{21}CH(OMe)_2$ with PhSeH in $CDCl_3$ showed (NMR control) the formation of 1-methoxy-1-(phenylseleno)undecane after addition of TFA. 1,1-Bis(phenylseleno)undecane was not detected [with amounts of TFA up to 81 mol % (based on starting acetal)]. The exchange between $C_{10}H_{21}CH(OMe)_2$ and **5** and **6** was followed (under similar conditions of temperature and concentration) by NMR. By use of 3 mol % of TFA with **5** the reaction time is greater than 12 h although 1-methoxy-1-(phenylseleno)undecane is formed quickly. By use of 1.8 mol % of TFA with **6** the reaction time is less than 20 min.
(28) Structures i and/or ii are chemically reasonable possibilities for the initial species.



(29) Jensen, J. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 1476.
(30) Treatment of $C_{10}H_{21}CHO$ with PhSeH in $CDCl_3$ showed (NMR control) formation of 1,1-bis(phenylseleno)undecane provided substantial amounts [we used up to 134 mol % (based on aldehyde)] of TFA are employed. These conditions are reminiscent of those in ref 6.

Table I

	product[a]	time	mol % TFA[b]	yield, %
10		3 h	3.8	48
11		20 min	4.0	96
12		3.5 h	5.6	58
13		2.5 h 40 min	0 10.2	89 88
14		24 h 1 h	0 8.6	84 63
15		18 h	3.4	~80
16		50 min	4.3	90
17	$Bu_2C(SePh)_2$	14 h 1 h	trace TsOH·H_2O 10.6	80 73
18	$Bu_2C(SeMe)_2$	45 min	7.8	90
19		26 h	19	79[c]
20	$C_{10}H_{21}CH(SePh)_2$	4 h 1 h	trace TsOH·H_2O 7	78 79
21	$C_{10}H_{21}CH(SeMe)_2$	31 h	66	66
22		35 min	4.6	92
23		3.5 h	2.2	28[d]
24		1 h	9	52[d]
25		2 h	4.1	85
26		19 h	26.5	31[c,e]
27	$MeC(SeM)_3$[f]	13 h	7.5	39

[a] Unless otherwise stated the starting material is the corresponding ketone or aldehyde. [b] Percent based on carbonyl substrate. [c] See Experimental Section for evidence of structure. [d] Good yields can be obtained by acetal exchange.[5] [e] In an attempt to prepare the bis(phenylseleno)acetal, we obtained a complex mixture. [f] This is an exchange experiment; the starting material is $CH_3C(OMe)_3$. The corresponding exchange[5] with $B(SePh)_3$ is very slow.

(cf. the formation of **23** and **25**). (iii) Neither borane reagent is appropriate for cholest-4-en-3-one. (iv) On the basis of a single example (8-*tert*-butyl-1,4-dithiaspiro[4.5]decane[5]) the dithio ketal group is inert to both borane reagents in the presence of TFA. (v) Sulfoxides are deoxygenated by both borane reagents[31] in the absence of acid, and this reduction can be performed in the presence of a carbonyl group.

(31) See literature cited in ref 25.

Experimental Section

The borane reagents were handled as described in the text, and reactions were conducted under anhydrous conditions in a septum-closed flask whose contents were stirred magnetically and kept under a slight static pressure of nitrogen. All solvents were distilled before use. Dry CH_2Cl_2 and toluene were distilled from

CaH_2, dry $CHCl_3$ was distilled from P_2O_5 (under N_2), and dry pentane was distilled from $LiAlH_4$. During product isolation, solutions were dried over Na_2SO_4 and evaporated under water-pump vacuum at room temperature. Where products were isolated simply by evaporation of their solutions, the residues were kept under oil-pump vacuum and checked for constancy of weight. Except where noted, isolated bulk products were submitted directly for combustion analysis without additional purification. Plates for PLC were 60 × 20 × 0.1 cm and were heated at 110 °C for 1 h before use. Alumina for PLC and TLC was Merck Type GF-254 (Type 60/E), and silica gel was Merck Type 60-PF-254. Alumina for column chromatography was Camag neutral aluminum oxide of Brockmann activity 3. NMR spectra were measured on a 100-MHz instrument at a probe temperature of 32 °C. Small satellite signals are not reported. IR spectra of all compounds were unexceptional. Mass spectra were run at an ionizing voltage of 70 eV. Boiling points quoted for products distilled in a Kugelrohr apparatus refer to the oven temperature.

Tris(phenylseleno)borane (5).[20] This compound was made by the following procedure using an oven-dried apparatus that was allowed to cool with a slow stream of dry nitrogen passing through it. Passage of nitrogen was continued throughout the experiment. The reagents and solvents were dispensed by syringe. Boron tribromide (14.32 g, 57.1 mmol) was placed in a 250-mL three-necked flask equipped with a pressure-equalizing addition funnel, a magnetic stirring bar, and a double-walled condenser closed with a rubber septum. The flask was cooled in an ice bath, and the stirrer was started. Carbon disulfide (100 mL; dried by distillation from P_2O_5) was injected into the flask, and a solution of benzeneselenol[32] (26.95 g, 17.16 mmol) in dry CS_2 (50 mL) was added from the addition funnel over a 4-h period. The ice bath, and hence the solution, was then allowed to warm to room temperature, and stirring was continued overnight. The septum on the condenser was replaced by a vacuum takeoff with a tap which was connected in series to a large trap cooled in dry ice–ethanol, a tube packed with anhydrous calcium sulfate, and a water pump. Passage of nitrogen was stopped, and the solvent was evaporated. The residual yellow solid was suspended in dry pentane (100 mL), and the stirred mixture was refluxed for 4 h under a slight static pressure of nitrogen. The mixture was cooled slightly, and the yellow supernatant was removed by syringe. This procedure was repeated with two more portions (each 100 mL) of pentane. The resulting off-white solid was dried under vacuum. The material weighed 20.48 g (74%). It was sealed in ampules for prolonged storage.

Dimethyl Diselenide.[22] This compound was prepared in a fume hood. Selenium powder (27.39 g, 347 mmol) and $NaBH_4$ (9.13 g, 242 mmol) were placed in a 1-L flask equipped with a magnetic stirring bar, a pressure-equalizing addition funnel charged with absolute EtOH (500 mL), and a double-walled condenser closed with a septum. The latter carried inlet and exit needles for nitrogen. The EtOH was added over 2 h, with stirring, to the Se–$NaBH_4$ mixture. Ice-bath cooling was required to control the resulting vigorous reaction. The mixture was refluxed for 1.5 h and was then cooled to ~0 °C. MeI (55.0 g, 387.5 mmol) was added in one portion with stirring, and stirring was continued overnight. The mixture was partitioned between water (300 mL) and pentane (200 mL). The dark yellow pentane layer was washed with water (2 × 1 L). The initial aqueous phase (containing most of both the ethanol and the 300-mL portion of water) was extracted with pentane (300 mL), and this organic extract was washed once with water (200 mL). The pentane layers were combined and dried, and dimethyl diselenide (15.62 g, 47%) was isolated by distillation as a bright yellow liquid suitable for the next stage; bp 55–60 °C (~50 mm).

Tris(methylseleno)borane (6).[21] This compound was prepared under a slight static pressure of nitrogen. Dimethyl diselenide (15.62 g, 83 mmol) was added to commercial dry Et_2O (200 mL) contained in a 500-mL flask carrying a double-walled condenser fitted with a septum (which was used for introduction of nitrogen). The ether solution was stirred magnetically and cooled to about −80 °C by a dry ice–acetone bath. $LiAlH_4$ (1.80 g, 47.5 mmol) was added in one portion, and the mixture was stirred for 72 h, the cold bath being allowed to attain room temperature during the first 2–3 h. After the 3-day period $BF_3{\cdot}Et_2O$ (8.40 g, 59.2 mmol) was injected through the septum at the top of the condenser, and the suspension was refluxed with stirring for 6 h. The mixture was cooled and volatile material was evaporated at room temperature by using an oil pump and a large trap cooled by liquid nitrogen. The residual gray sludge was then distilled (behind a safety shield) under oil-pump vacuum and with an oil bath that was taken up to 120 °C. Tris(methylseleno)borane (12.56 g, 77%) was obtained as a pale yellow liquid: bp 83–85 °C (0.1 mm); NMR ($CDCl_3$) δ 2.17 (s). The material solidifies when stored at −10 °C.

1,1-Bis(phenylseleno)cyclopentane (10). Cyclopentanone (145 mg, 1.73 mmol) was injected into a stirred solution of tris(phenylseleno)borane (583 mg, 1.22 mmol) in $CHCl_3$ (3 mL). TFA (5 μL, 0.065 mmol) was added. After 3 h[33] the solvent was evaporated, and the residue was dissolved in MeOH (3 mL). $NaBH_4$ was added in small portions to the stirred solution until the yellow color was discharged. The mixture was immediately partitioned between pentane (50 mL) and 5% w/v aqueous Na_2CO_3 (50 mL). The pentane layer was washed once with water, dried, and evaporated. Chromatography of the residue over alumina (3 × 5 cm) with pentane gave 319 mg (48%) of **10** as a white, homogeneous (TLC, alumina, pentane) solid: NMR ($CDCl_3$) δ 1.4–2.2 (m, 8 H), 7.1–7.5 (m, 6 H), 7.5–7.9 (m, 4 H); exact mass *m/e* 225.0153 [calcd for $C_{11}H_{13}{}^{80}Se$ (M − PhSe), *m/e* 225.0182]. No further purification was needed for analysis. Anal. Calcd for $C_{17}H_{18}Se_2$: C, 53.70; H, 4.77. Found: C, 53.90; H, 4.85. Crystallization from 2:1 methanol–acetone gave plates, mp 73–75 °C.

1,1-Bis(methylseleno)cyclopentane (11). Cyclopentanone (138 mg, 1.64 mmol) was injected into a stirred solution of tris(methylseleno)borane (352 mg, 1.20 mmol) in $CHCl_3$ (2 mL). TFA (5 μL, 0.065 mmol) was added, and an *immediate* precipitate formed on the walls of the reaction flask. After an arbitrary period of 20 min the solvent was evaporated, and the residue was diluted with MeOH (2 mL). $NaBH_4$ was added in small portions to the stirred solution until the yellow color was discharged. The mixture was immediately partitioned between pentane (50 mL) and 5% w/v aqueous Na_2CO_3 (50 mL). The pentane layer was washed once with water, dried, and evaporated. Kugelrohr distillation gave 405 mg (96%) of **11** as a colorless, homogeneous (TLC, alumina, hexane) liquid: bp 93 °C (0.6 mm); NMR ($CDCl_3$) δ 1.6–2.2 (m, incorporating a singlet at 1.99); exact mass *m/e* 257.9437 (calcd for $C_7H_{14}{}^{80}Se_2$, *m/e* 257.9426). Anal. Calcd for $C_7H_{14}Se_2$: C, 32.83; H, 5.51. Found: C, 32.93; H, 5.51.

3-Methoxy-17,17-bis(methylseleno)estra-1,3,5(10)-triene (12). Tris(methylseleno)borane (239 mg, 0.82 mmol) and then TFA (5 μL, 0.068 mmol) were injected into a stirred solution of estrone methyl ether (345 mg, 1.21 mmol) in $CHCl_3$ (4 mL). After 3.5 h only a trace of the starting ketone was detectable by TLC (silica, $CHCl_3$). The mixture was partitioned between water (50 mL) and $CHCl_3$ (50 mL). The organic layer was dried and evaporated. The residue was dissolved in hot acetone (8 mL), and the solution was cooled to afford crystals (batch A). More of the desired product was isolated from the mother liquors by chromatography over silica (2 × 40 cm) with 1:1 benzene–hexane. Batch A was recrystallized from acetone (10 mL) to afford 127.1 mg (batch B) of **12** (mp 134–135 °C). The material from the chromatography was recrystallized from the mother liquors from batch B. A further crop (65.9 mg, mp 133–135 °C; batch C) of **12** was obtained, and the mother liquors from this batch C gave a final portion (127.7 mg, mp 133–135 °C) of **12** when concentrated and crystallized from acetone (1.5 mL). The total yield of **12** amounted to 320.7 mg (58%). Material from another similar experiment was analyzed after crystallization from acetone: NMR ($CDCl_3$) δ 0.85–2.95 (m, incorporating a singlet at 1.02 and two partially resolved singlets at 2.02, 24 H), 3.72 (s, 3 H), 6.5–6.8 and 7.05–7.28 (m, 3 H); exact mass *m/e* 362.1148 [calcd for $C_{20}H_{26}OSe$ (M − MeSeH), *m/e* 362.1149]. Anal. Calcd for $C_{21}H_{30}OSe_2$: C, 55.26; H, 6.63; O, 3.51. Found: C, 55.51; H, 6.75; O, 3.80.

3,3-Bis(phenylseleno)-5α-cholestane (13). (a) Without Acid Catalysis. A solution of 5α-cholestan-3-one (160 mg, 0.42

(32) "Organic Syntheses", Collect. Vol. III; Wiley: New York, 1965; p 771.

(33) The reaction period was arbitrary and was suggested by the bulk of the precipitate that formed. No increase in yield was achieved by extending the period to 24 h.

mmol) in CH_2Cl_2 (1 mL) was injected over 10 min to a stirred suspension of tris(phenylseleno)borane (131 mg, 0.27 mmol) in CH_2Cl_2 (2 mL) that was cooled by a bath set at −30 °C. More CH_2Cl_2 (2 × 5 mL) was used to rinse all the ketone from its initial containing flask into the reaction vessel. After 30 min considerable ketone was still present (TLC). The reaction vessel was allowed to warm to room temperature (over about 1 h) and was left at room temperature for a further 1 h, by which time no starting ketone remained (TLC). The solvent was evaporated, and chromatography of the residue over alumina (2 × 20 cm) with pentane afforded 252 mg (89%) of **13** as a homogeneous (TLC, alumina, pentane) oil: NMR ($CDCl_3$) δ 0.2–2.2 (m, incorporating 2 br s at 0.35 and 0.56, 46 H), 7–7.9 (m, 10 H). The material was identical with a sample made[17a] by treating an ethereal mixture of 5α-cholestanone and benzeneselenol with HCl gas. The latter sample had exact mass *m/e* 526.3069 [calcd for $C_{33}H_{50}{}^{80}Se$ (M − PhSe), *m/e* 526.3078] and was analyzed. Anal. Calcd for $C_{39}H_{56}Se_2$: C, 68.60; H, 8.27. Found: C, 68.67; H, 8.27.

(b) With Acid Catalysis. A solution of 5α-cholestan-3-one (98 mg, 0.25 mmol) in $CHCl_3$ (0.5 mL) was injected with stirring into a flask containing tris(phenylseleno)borane (82 mg, 0.17 mmol). More $CHCl_3$ (2 × 0.5 mL) was used to rinse the ketone from its initial containing flask into the reaction vessel. TFA (2 μL, 0.026 mmol) was added to the reaction mixture. No ketone remained after 40 min (TLC). The solution was placed on a column (1 × 3 cm) of alumina. Elution with $CHCl_3$ (50 mL) gave a crude product which was purified by PLC (one alumina plate developed with pentane). The appropriate band was eluted with $CHCl_3$ to afford 152 mg (88%) of **13** as a homogeneous (TLC, alumina, pentane) oil identical with an authentic specimen.[17a]

2,2-Bis(phenylseleno)tricyclo[3.3.1.1^{3,7}]decane (14). (a) Without Acid Catalysis. Tricyclo[3.3.1.1^{3,7}]decan-2-one (66 mg, 0.44 mmol) in $CHCl_3$ (0.5 mL) was injected with stirring into a flask containing tris(phenylseleno)borane (149 mg, 0.311 mmol). More $CHCl_3$ (2 × 0.5 mL) was used to rinse the contents of the syringe into the reaction vessel. After a reaction period of 24 h the mixture was applied to a column of alumina (1.5 × 3 cm) made up with $CHCl_3$. More $CHCl_3$ (150 mL) was passed through the column, and the eluate was evaporated. The product was separated by PLC (one alumina plate developed with pentane). The appropriate band was eluted with $CHCl_3$, and the solution was evaporated to give 165 mg (84%) of **14** as a homogeneous (TLC, alumina, pentane), colorless solid: mp 152–155 °C; NMR ($CDCl_3$) δ 1.44–2.20 (m, 10 H), 2.6–3.0 (m, 4 H), 7.12–7.45 (m, 6 H), 7.62–7.9 (m, 4 H). Analytically pure material from a different experiment[17a] had mp 153–154 °C; exact mass *m/e* 291.0648 [calcd for $C_{16}H_{19}{}^{80}Se$ (M − PhSe), *m/e* 291.0652]. Anal. Calcd for $C_{22}H_{24}Se_2$: C, 59.20; H, 5.42. Found: C, 59.32; H, 5.44.

(b) With Acid Catalysis. Tricyclo[3.3.1.1^{3,7}]decan-2-one (45.4 mg, 0.302 mmol) in $CHCl_3$ (0.5 mL) was injected with stirring into a flask containing tris(phenylseleno)borane (96.5 mg, 0.202 mmol). More $CHCl_3$ (2 × 0.5 mL) was used to rinse the contents of the syringe into the reaction vessel. TFA (2 μL, 0.026 mmol) was injected immediately. After 1 h the reaction mixture was applied to a column of alumina (1 × 3 cm) made up with $CHCl_3$. More $CHCl_3$ (50 mL) was passed through the column, and the eluate was evaporated. The product was separated by PLC (one alumina plate developed with pentane). The appropriate band was eluted with $CHCl_3$, and the solution was evaporated to give 85.5 mg (63%) of **14**, mp 152–155 °C.

4-*tert*-Butyl-1,1-bis(phenylseleno)cyclohexane (15). 4-*tert*-Butylcyclohexanone (292 mg, 1.90 mmol) in $CHCl_3$ (1 mL) was injected into a stirred solution of tris(phenylseleno)borane (618 mg, 1.29 mmol) in $CHCl_3$ (2 mL). Three portions (0.5 mL each) of $CHCl_3$ were used to rinse the contents of the syringe into the reaction vessel. TFA (5 μL, 0.65 mmol) was then added to the mixture. After 18 h the solvent was evaporated, and the residue was dissolved in a mixture of methanol (3 mL) and benzene (3 mL). $NaBH_4$ was added in small portions to the stirred solution until only a very pale yellow color pesisted. The mixture was immediately partitioned between pentane (100 mL) and 5% w/v aqueous Na_2CO_3 (50 mL). The organic layer was washed once with water, dried, and evaporated. Chromatography of the residue over alumina (3 × 50 cm) with pentane and removal of the solvent gave 686 mg (80%) of **15** as a pale yellow, homogeneous (TLC, alumina, pentane), and analytically pure (despite an 8 °C melting range) solid: mp 81–89 °C; NMR ($CDCl_3$) δ 0.6–2.25 (m, incorporating a singlet at 0.8, 18 H), 7.1–7.95 (m, 10 H); exact mass *m/e* 452.0543 (calcd for $C_{22}H_{28}{}^{80}Se_2$, *m/e* 452.0521). Anal. Calcd for $C_{22}H_{28}Se_2$: C, 58.67; H, 6.27. Found: C, 58.66; H, 6.30. Crystallization from 2:1 methanol–acetone gave plates, mp 89–91 °C.

4-*tert*-Butyl-1,1-bis(methylseleno)cyclohexane (16). 4-*tert*-Butylcyclohexanone (233 mg, 1.51 mmol) in $CHCl_3$ (1 mL) was injected with stirring into a flask containing tris(methylseleno)borane (310 mg, 1.06 mmol). Two portions (0.5 mL each) of $CHCl_3$ were used to rinse the contents of the syringe into the reaction vessel. TFA (5 μL, 0.065 mmol) was added to the mixture. A precipitate formed immediately. After an arbitrary period of 50 min the solvent was evaporated, and the residue was dissolved in MeOH (2 mL). $NaBH_4$ was added in small portions to the stirred solution until the yellow color was discharged. The mixture was immediately partitioned between pentane (70 mL) and 5% w/v aqueous Na_2CO_3 (50 mL). The pentane layer was washed once with water, dried, and evaporated. Kugelrohr distillation gave 446 mg (90%) of **16** as a colorless, homogeneous (TLC, alumina, pentane) liquid: bp 95 °C (0.025 mm); NMR ($CDCl_3$) δ 0.86 (s, 9 H), 1.5–2.2 (m, incorporating two singlets at 1.90 and 1.97, 15 H); exact mass *m/e* 328.0211 (calcd for $C_{12}H_{24}{}^{80}Se_2$, *m/e* 328.0209). Anal. Calcd for $C_{12}H_{24}Se_2$: C, 44.18; H, 7.42. Found: C, 44.02; H, 7.42.

5,5-Bis(phenylseleno)nonane (17).[5] (a) Use of *p*-Toluenesulfonic Acid. Nonan-5-one (98 mg, 0.69 mmol) and then one crystal of *p*-toluenesulfonic acid monohydrate were added to a stirred solution of tris(phenylseleno)borane (231 mg, 0.48 mmol) in $CHCl_3$ (3 mL). Some ketone appeared to be present (TLC) after 2 h. After an overnight reaction period the solvent was evaporated, and the product was separated by PLC (one alumina plate developed with pentane). The appropriate band was eluted with $CHCl_3$. Evaporation afforded 242 mg (80%) of **17** as a homogeneous (TLC, alumina, pentane) oil, identical with a sample made by using TFA.

(b) Use of TFA. Nonan-5-one (35 mg, 0.24 mmol) and then TFA (2 μL, 0.026 mmol) were injected into a stirred solution of tris(phenylseleno)borane (76 mg, 0.16 mmol) in $CHCl_3$ (2 mL). After an arbitrary period of 1 h the mixture was applied to a column of alumina (1 × 3 cm) made up with $CHCl_3$. More $CHCl_3$ (60 mL) was passed through the column, and the eluate was evaporated. The product was separated by PLC (one alumina plate developed with pentane). The appropriate band was eluted with $CHCl_3$. Evaporation of the solvent gave 79 mg (73%) of **17** as a colorless, analytically pure oil. Anal. Calcd for $C_{21}H_{28}Se_2$: C, 57.54; H, 6.44. Found: C, 57.50; H, 6.49.

5,5-Bis(methylseleno)nonane (18). Tris(methylseleno)borane (207 mg, 0.71 mmol) and then TFA (6 μL, 0.077 mmol) were injected into a stirred solution of nonan-5-one (142 mg, 1.00 mmol) in $CHCl_3$ (3 mL). The mixture became warm, and a faint yellow color developed. After 15 min the reaction appeared to be complete (TLC control), but, as the starting ketone does not show up well on TLC plates, the mixture was arbitrarily left for a further 30 min. It was then evaporated, and the residue was placed onto a small column (1 × 2 cm) of alumina made up with hexane. The appropriate fractions (TLC, alumina, heptane) were combined and evaporated. The resulting oil was distilled in a Kugelrohr apparatus to afford 285 mg (90%) of analytically pure **18** as a colorless liquid: bp 80 °C (0.1 mm); NMR ($CDCl_3$) δ 1.8–2.1 (m, incorporating a sharp singlet at 1.95); exact mass *m/e* 316.0220 (calcd for $C_{11}H_{24}{}^{80}Se_2$, *m/e* 316.0209). Anal. Calcd for $C_{11}H_{24}Se_2$: C, 42.04; H, 7.70. Found: C, 42.17; H, 7.93.

3β-Acetoxy-20,20-bis(methylseleno)pregn-5-ene (19). Tris(methylseleno)borane (294 mg, 1.01 mmol) and then TFA (20 μL, 0.26 mmol) were injected into a stirred solution of 3β-acetoxypregn-5-en-20-one (513 mg, 1.43 mmol) in $CHCl_3$ (5 mL). After 26 h at room temperature only a trace of starting ketone was detectable by TLC (silica, $CHCl_3$). The mixture was partitioned between $CHCl_3$ (20 mL) and water (10 mL), and the organic phase was dried and evaporated. The residue was purified by column chromatography over silica gel (3 × 30 cm column; elution with $CHCl_3$). Appropriate fractions were combined and evaporated to afford 655 mg of **19**. Recrystallization from a mixture of acetone (1 mL) and MeOH (5 mL) gave 606 mg (79%) of **19** as a white homogeneous (TLC, silica, $CHCl_3$) solid: mp 153–156 °C. A

portion (85.3 mg) was recrystallized from EtOAc (1.5 mL) to give 62.4 mg of **19**: mp 159–161 °C; IR ($CHCl_3$) 1722 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.7 (m, 38 H), 4.35–4.80 (m, 1 H), 5.25–5.45 (m, 1 H); exact mass m/e 437.1972 [calcd for $C_{24}H_{37}O_2{}^{80}Se$ (M – MeSe), m/e 437.1958]. Satisfactory analytical data could not be obtained for this compound. Supporting evidence for the structure comes from the properties of the product obtained[34] (73%) by Ph_3SnH reduction:[17a] mp 148–149; $[\alpha]^{25}_D$ –61.16° (c 0.5, $CHCl_3$). 3β-Acetoxypregn-5-ene has mp 147–148 and $[\alpha]^{25}_D$ –62° (c 3.66, $CHCl_3$).[35]

1,1-Bis(phenylseleno)undecane (20).[6] **(a) Use of *p*-Toluenesulfonic Acid.** Undecanal (114 mg, 0.67 mmol) and then *p*-toluenesulfonic acid monohydrate (ca. 0.1 mg) were added to a stirred solution of tris(phenylseleno)borane (222 mg, 0.46 mmol) in $CHCl_3$ (3 mL). After an arbitrary period of 4 h the solvent was evaporated, and the product was separated by PLC (one alumina plate developed with pentane). The appropriate band was eluted with $CHCl_3$, and the solution was evaporated to yield 243 mg (78%) of **20** as a homogeneous (TLC, alumina, pentane) oil: NMR ($CDCl_3$) δ 0.7–2.12 (m, 21 H), 4.45 (t, 1 H, J = 6.4 Hz), 7.1–7.34 (m, 6 H), 7.38–7.66 (m, 4 H); exact mass m/e 468.0382 (calcd for $C_{23}H_{32}{}^{80}Se_2$, m/e 468.0834).

(b) Use of TFA. Undecanal (62 mg, 0.364 mmol) and then TFA (2 μL, 0.026 mmol) were injected into a stirred solution of tris(phenylseleno)borane (122 mg, 0.25 mmol) and $CHCl_3$ (2 mL). After an arbitrary period of 1 h the mixture was applied to a column (1 × 3 cm) of alumina made up with $CHCl_3$. More $CHCl_3$ (50 mL) was passed through the column, and the eluate was evaporated. The product was separated by PLC (one alumina plate developed with pentane). The appropriate band was eluted with $CHCl_3$, and the solution was evaporated to afford 135 mg (79%) of **20**[6] as a colorless oil identical with material made by using *p*-toluenesulfonic acid.

1,1-Bis(methylseleno)undecane (21). Tris(methylseleno)borane (180 mg, 0.61 mmol) and then TFA (5 μL, 0.065 mmol) were injected into a stirred solution of undecanal (150 mg, 0.88 mmol) in $CHCl_3$ (5 mL). After 28 h at room temperature a further portion (40 μL, 0.519 mmol) of TFA was added. After a further 3 h the composition of the mixture appeared to be static (TLC). The solvent was removed, and the residue was dissolved in MeOH (2 mL). $NaBH_4$ was added in small portions to the stirred solution until the yellow color was discharged. The mixture was immediately partitioned between pentane (60 mL) and 5% w/v aqueous Na_2CO_3 (50 mL). The pentane layer was dried and evaporated. Kugelrohr distillation gave 201 mg (66%) of **21** as a pale yellow, homogeneous (TLC, alumina, hexane) liquid: bp 108 °C (0.025 mm); NMR ($CDCl_3$) δ 0.7–2.2 (m, incorporating a s at 2.0, 27 H), 3.9 (t, J = 7 Hz, 1 H); exact mass m/e 344.0532 (calcd for $C_{13}H_{28}{}^{80}Se_2$, m/e 344.0522). Anal. Calcd for $C_{13}H_{28}Se_2$: C, 45.62; H, 8.24. Found: C, 45.78; H, 8.32. When the above experiment was repeated in an NMR tube but with the initial relative proportion of TFA increased 8.3-fold [i.e., TFA (10 μL) with undecanal (0.212 mmol) in $CDCl_3$ (ca. 0.5 mL, containing tris(methylseleno)borane (0.144 mmol))], the reaction appeared to be complete within 2.5 h.

1-[Bis(methylseleno)methyl]naphthalene (22). Tris(methylseleno)borane (236 mg, 0.81 mmol) was injected into a stirred solution of 1-naphthaldehyde (176 mg, 1.13 mmol) in $CHCl_3$ (5 mL). Heat was generated, but the solution remained clear. TFA (4 μL, 0.052 mmol) was added 5 min after mixing, and a bulky precipitate formed immediately. After an arbitrary additional period of 30 min the mixture was partitioned between $CHCl_3$ (60 mL) and water (50 mL). The organic layer was dried and evaporated. Chromatography of the residue over alumina (3 × 10 cm) with 1:99 benzene–hexane gave 343 mg (92%) of **22** as a colorless and homogeneous (TLC, alumina, 5:95 benzene–hexane) liquid: NMR ($CDCl_3$) δ 1.97 (s, 6 H), 5.8 (br s, 1 H), 7.2–7.95 (7, 6 H); exact mass m/e 329.9435 (calcd for $C_{13}H_{14}{}^{80}Se_2$, m/e 329.9426). Anal. Calcd for $C_{13}H_{14}Se_2$: C, 47.58; H, 4.30. Found: C, 47.50; H, 4.33.

1-(2-Naphthyl)-1,1-bis(phenylseleno)ethane (23). 2′-Acetylnaphthalene (104 mg, 0.61 mmol) in $CHCl_3$ (0.5 mL) was injected into a stirred solution of tris(phenylseleno)borane (202 mg, 0.42 mmol) in $CHCl_3$ (1.5 mL). More $CHCl_3$ (2 × 0.5 mL) was used to rinse all the ketone from its initial container into the reaction vessel. TFA (1 μL, 0.013 mmol) was added to the mixture, resulting in the formation of a deep red color. After 3.5 h a trace of ketone remained.[36] The solvent was evaporated, and **23** was isolated as a yellow oil (98.5 mg, 34%) by chromatography over alumina (1 × 50 cm) with 99:1 hexane–ethyl acetate. Crystallization from hexane (1 mL) gave 82 mg (28%) of **23** as a solid: mp 86–91 °C. Pure material[5] has mp 88–92 °C.

[1,1-Bis(phenylseleno)ethyl]benzene (24). Acetophenone (35 mg, 0.29 mmol) and then TFA (2 μL, 0.026 mmol) were injected into a stirred solution of tris(phenylseleno)borane (104 mg, 0.22 mmol) and $CHCl_3$ (2 mL). After an arbitrary period[37] of 1 h the mixture was applied to a column (1 × 3 cm) of alumina made up with $CHCl_3$. More $CHCl_3$ (50 mL) was passed through the column, and the eluate was evaporated. The product was separated by PLC (one alumina plate developed with pentane). The appropriate band was eluted with $CHCl_3$, and the solution was evaporated to afford 63 mg (52%) of **24** as a colorless, analytically pure oil.[5] Anal. Calcd for $C_{20}H_{18}Se_2$: C, 57.71; H, 4.36. Found: C, 57.72; H, 4.54.

1-(2-Naphthyl)-1,1-bis(methylseleno)ethane (25). Tris(methylseleno)borane (259 mg, 0.88 mmol) and then TFA (4 μL, 0.052 mmol) were injected into a stirred solution of 2-acetylnaphthalene (214 mg, 1.27 mmol) in $CHCl_3$ (5 mL). After 1 h only a trace of the ketone remained (TLC), and, after a further 1 h, the mixture was partitioned between $CHCl_3$ (30 mL) and water (30 mL). The organic layer was dried and evaporated. Chromatography of the residue over alumina (3 × 60 cm) with 49:1 hexane–ethyl acetate gave 369 mg (85%) of **25** as a pale yellow, homogeneous (TLC, alumina, 95:5 hexane–ethyl acetate) oil: NMR ($CDCl_3$) δ 1.9 (s, 6 H), 2.39 (s, 3 H), 7.35–7.60 (m, 2 H), 7.6–8.05 (m, 5 H); exact mass m/e 249.0163 [calcd for $C_{13}H_{13}{}^{80}Se$ (M – MeSe), m/e 249.0182). Anal. Calcd for $C_{14}H_{16}Se_2$: C, 49.14; H, 4.71. Found: C, 49.05; H, 4.58.

3,3-Bis(methylseleno)cholest-4-ene (26). Tris(methylseleno)borane (498 mg, 1.70 mmol) and then TFA (10 μL, 0.130 mmol) were injected into a stirred, ice-cold solution of cholest-4-en-3-one (942 mg, 2.45 mmol) in $CHCl_3$ (20 mL). After 1.5 h the pale yellow solution contained a considerable amount of starting ketone (TLC). The ice bath was removed, and TFA (40 μL, 0.519 mmol) was added. After a further 17.5 h very little starting material remained (TLC). The mixture was shaken with water (10 mL), dried, and evaporated. Chromatography of the residue over silica gel (3 × 50 cm) with hexane gave 433 mg (31%) of **26** as a colorless, homogeneous (TLC, alumina, hexane), but unstable oil that crystallized slowly at –10 °C: NMR ($CDCl_3$) δ 5.49 (br s, $w_{1/2}$ = 4 Hz, 1 H), 0.6–2.45 (m, incorporating singlets at 2.00 and 2.09, 49 H); exact mass m/e 462.2777 [calcd for $C_{28}H_{46}{}^{80}Se$ (M – CH_2Se), m/e 462.2751. Satisfactory analytical data were not obtained for this compound. Supporting evidence for the structure comes from the properties of the hydrocarbon obtained[34] (37%) by Ph_3SnH reduction:[17a] mp 78–79 °C; $[\alpha]^{25}_D$ +72.5° (c 1.18, $CHCl_3$); NMR ($CDCl_3$) δ 0.68 (s), 1.0 (s) (inter alia). Cholest-4-ene has[38] melting point values in the range 77–83 °C, $[\alpha]^{25}_D$ +71 ± 5°[38] (c 1–5, $CHCl_3$), and NMR ($CDCl_3$) δ inter alia 0.67 (s), 0.99 (s).[39]

1,1,1-Tris(methylseleno)ethane (27). Tris(methylseleno)borane (546 mg, 1.87 mmol) and then TFA (10 μL, 0.130 mmol) were injected into a stirred solution of 1,1,1-trimethoxy-

(34) Unpublished observations.

(35) Barton, D. H. R.; Holness, N. J.; Klyne, W. *J. Chem. Soc.* **1949**, 2456.

(36) No significant improvement was observed in extending the reaction period to 14 h.

(37) In a similar experiment carried out overnight the yield was 50%.

(38) Jacques, J.; Kagan, H.; Ourisson, G. "Tables of Constants and Numerical Data"; Allard, S., Ed.; Pergamon Press: Oxford, 1965; Vol. 14.

(39) Cragg, G. M. L.; Davey, C. W.; Hall, D. N.; Meakins, G. D.; Richards, E. E.; Whateley, T. L. *J. Chem. Soc. C* **1966**, 1266. A minor impurity was detectable by $AgNO_3$-impregnated TLC plates. The ^{13}C NMR spectrum corresponded band for band with the values reported for cholest-4-ene: Blunt, J. W.; Stothers, J. B. *Org. Magn. Reson.* **1977**, *9*, 439.

(40) For the chemistry of boron–sulfur species see: (a) Bessette, F.; Brault, J.; Lalancette, J. M. *Can. J. Chem.* **1965**, *43*, 307. (b) Cragg, R. H.; Husband, J. P. N. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 773. (c) Cohen, T.; Bennett, D. A.; Mura A. J., Jr. *J. Org. Chem.* **1976**, *41*, 2506. (d) Pelter, A.; Levitt, T. E.; Smith, K.; Jones, A. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1672.

ethane (209 mg, 1.74 mmol) in $CHCl_3$ (5 mL). After 13 h the solvent was evaporated. Chromatography of the residue over alumina (3 × 50 cm) with hexane gave 213 mg (39%) of the major product **27** as a homogeneous (TLC, alumina, hexane) oil: NMR ($CDCl_3$) δ 2.1 (s, 9 H), 2.23 (s, 3 H); exact mass *m/e* 311.8451 (calcd for $C_5H_{12}{}^{80}Se_3$, *m/e* 311.8435). For analysis the material was distilled in a Kugelrohr apparatus; bp 110 °C (20 mm). Anal. Calcd for $C_5H_{12}Se_3$: C, 19.43; H, 3.91. Found: C, 19.61; H, 3.73.

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Registry No. 5, 29680-62-4; **6**, 29634-51-3; **10**, 71518-65-5; **11**, 71518-66-6; **12**, 71518-67-7; **13**, 66729-72-4; **14**, 66729-73-5; **15**, 71518-68-8; **16**, 71518-69-9; **17**, 67808-79-1; **18**, 71518-70-2; **19**, 71518-71-3; **20**, 53198-55-3; **21**, 63017-80-1; **22**, 71518-72-4; **23**, 69470-14-0; **24**, 67808-80-4; **25**, 71518-73-5; **26**, 71518-74-6; **27**, 66622-21-7; boron tribromide, 10294-33-4; benzeneselenol, 645-96-5; dimethyl diselenide, 7101-31-7; selenium, 7782-49-2; methyl iodide, 74-88-4; cyclopentanone, 120-92-3; estrone methyl ether, 1624-62-0; 5α-cholestan-3-one, 566-88-1; tricyclo[3.3.1.1^{3,7}]decan-2-one, 700-58-3; 4-*tert*-butylcyclohexanone, 98-53-3; nonan-5-one, 502-56-7; 3β-acetoxypregn-5-en-20-one, 1778-02-5; 3β-acetoxypregn-5-ene, 3090-79-7; undecanal, 112-44-7; 1-naphthaldehyde, 66-77-3; 2′-acetylnaphthalene, 93-08-3; acetophenone, 98-86-2; cholest-4-en-3-one, 601-57-0; 1,1,1-trimethoxyethane, 1445-45-0.

Homoallyl and Cyclopropylcarbinyl Carbonium Ion Formations under Strongly Basic Conditions[1]

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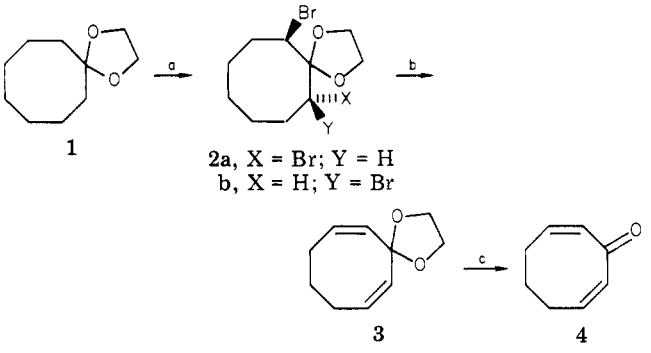
Treatment of *trans*-2,8-dibromocyclooctanone ethylene ketal with sodium hydroxide in refluxing methanol produced 2,7-cyclooctadienone ethylene ketal in yields of 71–79% and a mixture of 2-(2-cycloheptenyl)-2-methoxy-1,3-dioxolane (**15**) and 2-(*exo*-7-bicyclo[4.1.0]heptyl)-2-methoxy-1,3-dioxolane (**16**). The structures of the ortho ester side products were deduced from spectral and chemical methods. It was shown that the precursor of **15** was 2-bromocyclooct-7-enone ethylene ketal (**18**), and it was postulated that the intermediate which went on to **16** was 8-bromobicyclo[4.2.0]octan-7-one ethylene ketal (**25**). For the conversion of *trans*-2,7-dibromocycloheptanone ethylene ketal into the corresponding diene ketal, 2-(2-cyclohexenyl)-2-methoxy-1,3-dioxolane was found as a side product but not 2-(*exo*-6-bicyclo[3.1.0]hexyl)-2-methoxy-1,3-dioxolane. No rearrangement products were found with eliminations involving the ethylene ketals of *cis*-2,6-dibromo-4,4-dimethylcyclohexanone or *meso*-3,5-dibromo-4-heptanone. The involvement of intermediate carbonium ions is discussed.

In a previous report from this laboratory,[1b] it was shown that in the preparation of 2,7-cyclooctadienone (**4**) according to the reaction sequence developed by Garbisch (Scheme I),[2] the bis dehydrobromination step (**2** → **3**) was accompanied by interesting side reactions (apparently involving intermediate carbonium ions) which produced the ortho esters **15** and **16**. The structures of **15** and **16** were elucidated from spectral and analytical data, as well as from several chemical transformations (Schemes II and III).[3] Authentic samples of compounds **9** and **12** were prepared by independent routes,[4] while compounds **14a** and **14b** exhibited spectral properties identical with those reported for authentic materials.[5]

In a subsequent investigation, α,α'-dibromo ketals from the cycloheptyl and cyclohexyl frameworks as well as an acyclic system were subjected to the same elimination reaction conditions to find out what the effects of the smaller ring sizes would be on the side reactions. In this paper the results of that follow-up investigation are described; complete experimental details for the cyclooctyl system are also presented. Furthermore, additional information has been obtained which clarifies to some extent the origin of the ortho ester **16**.

Scheme I



a, Br_2/ether; b, NaOH/CH_3OH; c, 3% H_2SO_4.

Results

A. Cyclooctyl System. In the preliminary communication[1b] it was speculated that the homoallylic bromo ketal **18** (produced by the elimination of hydrogen bromide from dibromo ketal **2a**) ionized under the very polar reaction conditions to the homoallylic carbonium ion **19** and its cyclopropylcarbinyl counterpart **20**. Rearrangement of

(1) For a preliminary account of this work see: (a) Krabbenhoft, H. O. Abstracts, 8th Northeast Regional Meeting of the American Chemical Society, Boston, MA, June 25–28, 1978, No. ORGN 15. (b) Krabbenhoft, H. O. *J. Org. Chem.* **1978**, *43*, 4556.

(2) Garbisch, E. W., Jr. *J. Org. Chem.* **1965**, *30*, 2109.

(3) In actuality, mixtures of **5** and **6** were employed in the chemical degradations. Fortunately, in most cases the products resulting from reactions of **5** and **6** were separable and hence fully characterized; in those instances where separation was not achieved (i.e., with the carboxylic acids) the ^{13}C NMR spectra allowed definitive conclusions to be made.

(4) Karrer, P.; Keller, R.; Usteri, E. *Helv. Chim. Acta* **1944**, *27*, 237.

(5) (a) Musso, H. *Chem. Ber.* **1968**, *101*, 3710. (b) Ciganek, E. *J. Am. Chem. Soc.* **1971**, *93*, 2207. (c) Ishihara, T.; Ando, T.; Muranaka, T.; Saito, K. *J. Org. Chem.* **1977**, *42*, 666.

0022-3263/79/1944-4285$01.00/0