Synthesis and Reactions of Selenoketones

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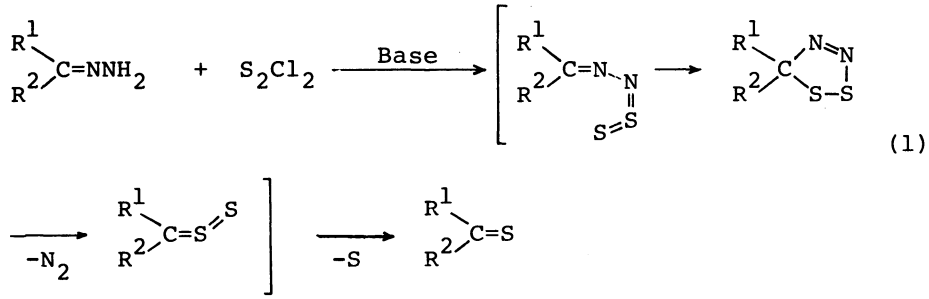
A new, convenient method for the synthesis of selenoketones has been reported. The reaction of dimagnesium salts of ketone hydrazones with diselenium dichloride affords an intermediate tentatively assigned as tetraselenides, which are converted into selenoketones by heating in the presence of tributylamine. A comparative study on the reactions of 1,1,3,3-tetramethyl-2-indanselone and the corresponding thioketone with Grignard and organolithium reagents have been carried out. Analysis of the reaction products has revealed that the heterophilic attack of the organometallic reagents is much more significant in the reaction with the selone than with the thione.

Organoselenium chemistry is of current interest[1] and considerable attention has been paid to the chemistry of selenoketones in recent years. They have been used as synthetic intermediates for hindered olefins[2] and their physical properties have been studied rather extensively.[3] Until our preliminary communication in 1983,[4] however, there had been known only two synthetic routes to these compounds, i.e., 1) the reaction of triphenylphosphoranylidenehydrazones with selenium metal above their melting points developed by Barton and his co-workers[2a] and 2) the reaction of ketones with bis(tricyclohexyltin) selenide in the presence of boron trichloride.[5] At almost the same time as with our communication, Guziec, Jr. and Moustakis reported the synthesis of selenoketones by the reaction of hydrazones with diselenium dibromide.[6] As for the reactions of selenoketones, some interesting examples have been reported,[2a,7] but the reactions with Grignard and organolithium reagents have not been reported. This is in contrast with thioketones because considerable attention has been paid in recent years to their reactions with organometallics which show unique heterophilic nature.[8] The purpose of this paper is to describe a full account of the synthesis of selenoketones and their reactions with organometallics.[9]

Results and Discussion

Synthesis of Selenoketones. 1) Method A. We previously reported the method for preparation of thioketones from the corresponding hydrazones and disulfur dichloride (Eq. 1).[10]



(1)

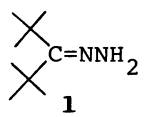
We became interested in whether this method would be applicable to selenoketone synthesis by using diselenium dichloride (Se_2Cl_2) instead of disulfur dichloride.

Optimization of the reaction conditions were carried out by using the reaction of di-*t*-butyl ketone hydrazone (**1**) with diselenium dichloride and the results are shown in Table 1. The maximum yield of di-*t*-butyl selenoketone (**2**) (28%) was obtained in benzene at 60 °C in the presence of 4-dimethylaminopyridine as tertiary base (Run 6).

Table 1. Reaction Conditions and Yields for Method A[a]

Run	Base(equiv)	Temp °C	Yield of 2 %
1	Et_3N(3.6)	5	7
2	DABCO[b](5.0)	5	11
3	*n*-Bu_3N(5.0)	5	17
4	DMAP[c](5.0)	5	21
5	DMAP(5.0)	r.t.	24
6	DMAP(5.0)	60	28
7	DMAP(5.0)	refl.	0

a) All reactions were carried out in benzene. b) 1,4-Diazabicyclo[2.2.2]octane. c) 4-Dimethylaminopyridine.



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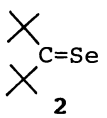

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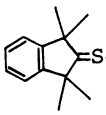
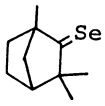
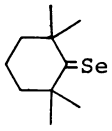
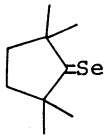
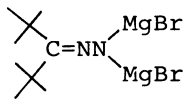
Table 2. Yields of Selenoketones by Methods A and B

Run	Selenoketone	Yield/%	
		Method A	Method B
1	(t-Bu)$_2$C=Se (**2**)	28	51(58)[a]
2	 (**3**)	31	82
3		7	24
4	(1-Ad)$_2$C=Se	24	53
5	(1-Ad)(t-Bu)C=Se		43
6		3	35
7		14	18

a) A yield obtained by the simultaneous addition method. b) 1-Ad denotes 1-adamantyl.

Under these optimized conditions some other selenoketones were synthesized and the results are summarized in Table 2. The yields of selenoketones by this method (Method A) are uniformly rather poor with a maximum (31%) for 1,1,3,3-tetramethyl-2-indanselone (**3**).

2) Method B. Since the yields by Method A were not satisfactory, we next attempted activation of hydrazones. Hydrazone **1** was converted to dimagnesium salt **4** by the reaction with 2 equiv of ethylmagnesium bromide in THF at 60 °C. After exchanging the solvent from THF to benzene, **4** was



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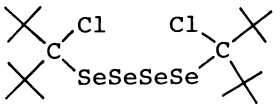
reacted with Se_2Cl_2 at room temperature in the presence of n-Bu_3N and the reaction solution was allowed to warm to 60 °C. Under these conditions selenoketone **2** was obtained in a 51% yield. The yields of other selenoketones were also increased (Table 2). If the reaction proceeds via a similar mechanism depicted in Eq. 1 for thioketones, a tertiary amine, tributylamine in this case, should be unnecessary. In the absence of tributylamine, however, only an orange material was obtained without formation of any selenoketone. This orange material, though stable during aqueous workup, was thermally not very stable and could not survive the chromatographic purification on silica gel, alumina, or Florisil undergoing decomposition with deposition of selenium. Although the instability did not permit further purification of this compound, its elemental analysis suggested the composition of $C_9H_{18}ClSe_2$. The ^{1}H NMR spectrum showed only one peak due to the t-butyl group at δ 1.4 and ^{77}Se NMR spectrum showed two peaks at 702 and 785 with almost comparable intensity along with some small peaks. On the basis of these data, the structure of the orange material is tentatively assigned as tetraselenide **5**, which would be converted into selenoketone **2** by treatment with tributylamine. Indeed, **2** was formed when a benzene solution of **5** was treated with tributylamine at 60 °C (60% yield based on **5**) or heated in vacuo (63% yield based on **5**). In contrast to this result it is interesting that Guziec, Jr. and Moustakis reported that 4H-1,2,3-selenadiazete **6** was an intermediate in the reaction of a



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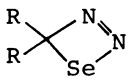

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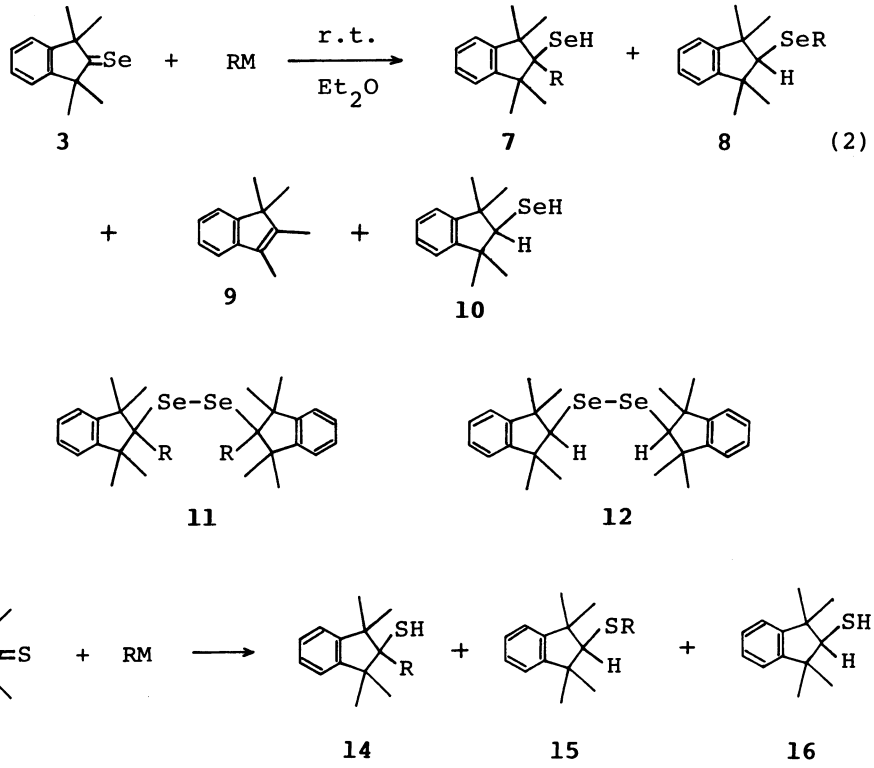
hydrazone and diselenium dibromide.[6] The formation mechanism of **5** is not clear at present. The formation of **5** was similarly observed in other selenoketone syntheses. Although the reactions of tributylamine with the tetraselenide were sometimes incomplete, selenoketones could be obtained by pyrolysis of the tetraselenide in vacuo in such cases.

The present method has some interesting features: (1) It provides selenoketones in a one-pot reaction unlike the Barton's method which requires isolation of the phosphoranylidenehydrazones. (2) Since the reaction is conducted under homogeneous conditions, there are none of the problems in a small scale synthesis encountered in the Barton's method where the reaction is conducted under heterogeneous conditions.[2a] (3) When two benzene solutions of dimagnesium salts of hydrazones and diselenium dichloride are added simultaneously and dropwise to a benzene solution of tributylamine, the yield is somewhat improved (Table 2, Run 1).

Reactions of 1,1,3,3-Tetramethyl-2-indanelone (3) with Grignard and Organolithium Reagents. Selenoketone **3** was selected for this investigation because **3** was obtained in a high yield and easily crystallized.

The reactions were carried out in ether at room temperature and four types of products **7**—**10** were isolated (Eq. 2). As **7** and **10** were easily oxidized to the corresponding diselenides in the air, their yields were determined after the conversion to diselenides **11** and **12**, respectively.



In order to compare the reactivity of the seleno- and thioketones, the reactions of the corresponding thioketone **13** with some organolithium reagents were also carried out under similar conditions (Eq. 3) to afford **14**—**16**. The results of these reactions are also shown in Table 3.

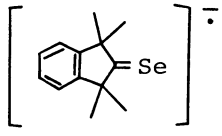
The products are classified as follows: (A) carbophilic addition products, **7** and **14**; (B) heterophilic addition products, **8**, **15**, and **9**; (C) reduction products, **10** and **16**. The results shown in Table 3 indicate that the reactions of organometallic reagents with selenoketone **3** are very unique in that the heterophilic nature is much more significant than those with thioketone **13**. Thus both selenophilic and carbophilic products were formed in the reaction of methyllithium with **3** whereas only the carbophilic product was formed for **13** (Run 1). The reaction of *t*-butyllithium with **3** (Run 3) gave some selenophilic product **8**, while **13** did not afford any thiophilic product. In the reaction with phenyllithium (Run 6) the preference of the heterophilic attack is even more obvious; the selenophilic product **8** was the sole product from **3** whereas the carbophilic product **14** was a main product from **13**. At the present time we do not have a definite answer to the question why the heterophilic nature is larger in the reaction of the selenoketone than in that of the thioketone. One possible explanation, however, is that the spin density in an intermediary anion radical (see below) is larger on selenium than on carbon.

Table 3. Reactions of **3** or **13** with Grignard or Organolithium Reagents

Run	RM	Yield/%						
		7[a]	**8**	**9**	**10**[a]	**14**	**15**	**16**
1	MeLi	73	10			91		
2	MeMgI	69						
3	*t*-BuLi		9		66			57
4	*t*-BuMgCl		15	22	44			
5	$PhCH_2Li$	86				95		
6	PhLi		47			56	24	
7	PhMgBr		3	14				

a) The yield was determined after the conversion to the corresponding diselenide.

Other interesting features are the formation of the reduction product **10** and 1,1,2,3-tetramethyl-1*H*-indene (**9**). It has been reported[8] that the reaction between thioketones and organometallic reagents bearing a β-hydrogen gave the reduction product. This has been explained in terms of the hydrogen abstraction of the anion radical formed by single electron transfer (SET) from the organometallic reagent to the thioketone. In the present reactions the reduction product **10** is obtained only in the reactions with *t*-BuLi and *t*-BuMgCl. This suggests that these reactions begin with a SET process giving anion radical I, which would abstract a hydrogen from a

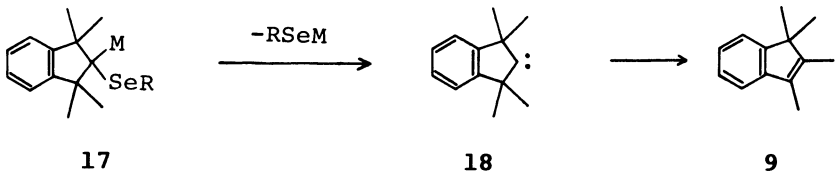


I

t-butyl radical to yield **10** (after protonation) and 2-methylpropene. Reactions with other Grignard and organolithium reagents also probably proceed via a SET process.

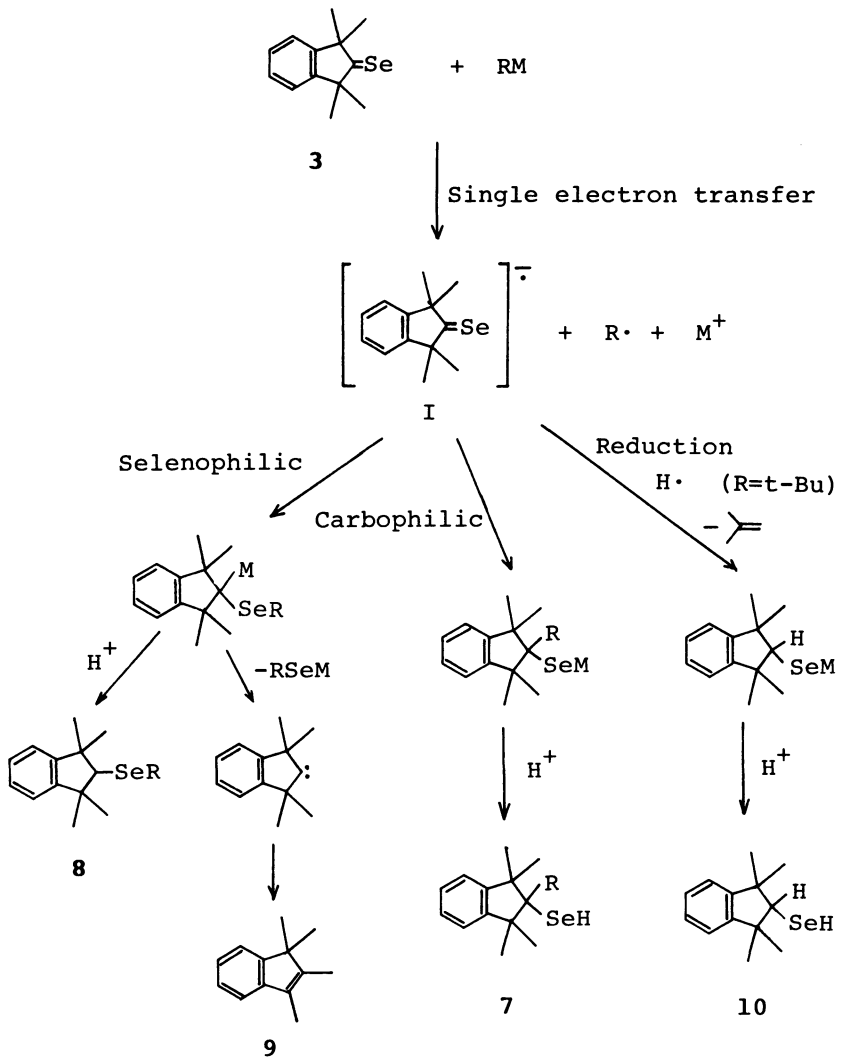
The formation of 1,1,2,3-tetramethyl-1*H*-indene (**9**) can be accounted for as shown in Scheme 1. Thus RSeM is eliminated from initially formed selenophilic adduct **17** to give carbene **18**, which then rearranges to **9**. There are some precedents of such carbene-forming reactions for sulfur-stabilized carbanions.[11] This type of elimination is known to occur when both a thioketone and an organometallic reagent are bulky and hence the cleavage of the intermediate is sterically accelerated and when the intermediate has a good leaving group. The present reactions of **3** with *t*-BuMgCl and PhMgBr meet these conditions: **3** is sterically crowded and the leaving group is either bulky (i.e., *t*-BuSe$^-$) or easily cleaved (i.e., PhSe$^-$). This type of carbene-forming reaction is, to our knowledge, the first example for selenoketones, although we recently reported a similar reaction between *O*-alkyl selenoformates and 2,4,6-tri-*t*-butylphenyllithium.[12]

The whole mechanistic scheme is shown in Scheme 2.



17 **18** **9**

Scheme 1.



Scheme 2.

Experimental

Melting points are uncorrected. ^1H(89.60 MHz) and ^{13}C(22.53 MHz) NMR spectra were measured in $CDCl_3$ with a JEOL FX-90Q spectrometer using tetramethylsilane as an internal standard. ^{77}Se NMR spectra were recorded at 17.09 MHz with a JEOL FX-90Q spectrometer, whose chemical shifts were measured in $CDCl_3$ with dimethyl selenide as an external standard. Infrared spectra were recorded on a Hitachi 260-30 infrared spectrometer. Ultraviolet and visible spectra were taken on a Hitachi 343 recording spectrophotometer. Mass and high-resolution mass spectra were obtained with a JEOL D-300 mass spectrometer. All reactions were carried out under an argon atmosphere.

Materials. Diselenium dichloride (Se_2Cl_2),[13] di-*t*-butyl ketone,[14] di-1-adamantyl ketone,[14] and 1-adamantyl *t*-butyl ketone hydrazones[14] were prepared by the reported method. The hydrazones of 1,1,3,3-tetramethyl-2-indanone, fenchone, 2,2,6,6-tetramethylcyclohexanone, and 2,2,5,5-tetramethylcyclopentanone were prepared from the corresponding ketones by the method of Barton.[15]

Syntheses of Selenoketones. General Procedure. 1) Method A. To 4-dimethylaminopyridine (5 mmol) in benzene (7 ml), preheated at 60 °C, were added simultaneously a hydrazone (1 mmol) in benzene (7 ml) and Se_2Cl_2 (1.5 mmol) in benzene (7 ml) at about the same rate by using two dropping funnels during 25 min. After stirring for 4 h at this temperature were added water and ether. Red-brown precipitates were removed by filtration and the yellow-green filtrate was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. Selenoketones in the residue were purified by silica-gel chromatography (hexane).

2) Method B. A THF (5 ml) solution of hydrazone (1 mmol) was added dropwise to ethylmagnesium bromide (2 mmol) in THF (5 ml) at 60 °C. The reaction occurred with evolution of ethane. After stirring for 1 h at this temperature, THF was removed under reduced pressure and benzene (80 ml) and tributylamine (1 mmol) were added. To this solution was added Se_2Cl_2 (1.2 mmol) in benzene (20 ml) at 5 °C during 20 min. Then the mixture was stirred at 60 °C for 3 h. After addition of water, the green-blue solution was washed with 2M HCl (1M=1 mol dm^{-3}) and water and dried over anhydrous $MgSO_4$. The residue obtained after the removal of the solvent under reduced pressure was heated at ca. 130 °C in vacuo (0.05 mmHg) (1 mmHg=133.322 Pa) in an apparatus with a cold trap. Crude selenoketones were purified by silica-gel chromatography (hexane). The yields of selenoketones by Methods A and B are listed in Table 1.

Di-*t*-butyl selenoketone,[3b,16] 1,1,3,3-tetramethyl-2-indanselone,[3b,7c] selenofenchone,[3b,16] and 2,2,5,5-tetramethylcyclopentaneselone[6] were identified by comparison of the chemical shifts of their ^1H and ^{13}C NMR spectra with their reported values.

Di-1-adamantyl Selenoketone: Blue crystals: mp 161—162 °C (hexane). ^1H NMR δ=1.61—1.81 (m, 12H), 1.92—2.21 (m, 6H), 2.21—2.42 (m, 12H); ^{13}C NMR δ=29.3, 36.6, 43.6, 63.7, 293.9 (C=Se, $^1J_{^{13}C-^{77}Se}$=209.0 Hz); ^{77}Se NMR δ=2134. IR(KBr) 2910, 2855, 1640, 1540, 1452, 1366, 1345, 1308, 1264, 1189, 1125, 1105, 1092, 1025, 1005, 982, 920, 825, 810, 736, 706, 670, 626 cm^{-1}. UV-VIS (cyclohexane) λ_{max} 712 nm (ε=23.7), 279 (6830), 239 (3990). Found: *m/z* 362.1511. Calcd for $C_{21}H_{30}{}^{80}Se$: M, 362.1513.

1-Adamantyl *t*-Butyl Selenoketone: Blue crystals; mp 39—41 °C (hexane). ^1H NMR δ=1.53 (s, 9H), 1.61—1.78 (m, 6H), 1.95—2.19 (m, 3H), 2.19—2.35 (m, 6H); ^{13}C NMR δ=29.2, 32.6, 36.6, 43.7, 60.4, 63.1, 292.9 (C=Se, $^1J_{^{13}C-^{77}Se}$=210.9 Hz); ^{77}Se NMR δ=2120. IR(KBr) 2900, 2845, 1636, 1535, 1472, 1444, 1392, 1358, 1342, 1308, 1258, 1216, 1180, 1118, 1096, 1046, 1028, 998, 946, 925, 818, 778, 715, 656, 634 cm^{-1}. UV-VIS (cyclohexane) λ_{max} 708 nm (ε=23.7), 274 (6920), 234 (3200). MS *m/z* 284(M^+), 227, 135 (base). Found: *m/z* 284.1064. Calcd for $C_{15}H_{24}{}^{80}Se$: M, 284.1043.

2,2,6,6-Tetramethylcyclohexaneselone: Blue liquid. ^1H NMR δ=1.41 (s, 12H), 1.81 (s, 6H);[6] ^{13}C NMR δ=18.3, 33.5, 38.4, 58.8, 294.4 (C=Se)[3d]; ^{77}Se NMR δ=2026 (lit,[3d] δ=2034); IR (neat) 3000, 2975, 2945, 2875, 1468, 1388, 1368, 1180, 1140, 1102, 1070, 1038, 1012, 990, 980, 952, 940, 882, 862, 778, 740, 668 cm^{-1}.[6] UV-VIS (cyclohexane) λ_{max} 686 nm (ε=24.3), 273 (6230), 227 (2300).[3d] Found: *m/z* 218.0582. Calcd for $C_{10}H_{18}{}^{80}Se$: M, 218.0572.

Reaction of Di-*t*-butyl Ketone Hydrazone (1) with Se_2Cl_2 in the Absence of Tributylamine. (a) Hydrazone **1** (63.0 mg, 0.403 mmol) was converted to bis(bromomagnesio)hydrazone **4** by Method B. This salt dissolved in benzene (6 ml) and Se_2Cl_2 (110 mg, 0.48 mmol) in benzene (6 ml) were simultaneously added to benzene (30 ml) at room temperature. The mixture was stirred at room temperature for 1 h. Water was added and the organic layer was washed with water and dried over anhydrous $MgSO_4$. The evaporation of the solvent gave an orange oil (88 mg), whose ^1H NMR spectrum showed a peak at δ 1.4 and the absense of di-*t*-butyl selenoketone. This orange oil was dissolved in benzene (40 ml) and tributylamine (0.12 g, 0.63 mmol) was added. After the resulting solution was stirred at 60 °C for 5 h, water was added. The organic layer was washed with 2M HCl and water and dried over anhydrous $MgSO_4$. From the residue obtained after the removal of the solvent, di-*t*-butyl selenoketone (24.8 mg, 30% based on the hydrazone) was collected in a cold trap in vacuo. (b) Hydrazone **1** (148 mg, 0.948 mmol) was converted to bis(bromomagnesio)hydrazone as described in Method B. This salt in benzene (5 ml) and Se_2Cl_2 (260 mg, 1.14 mmol) in benzene (5 ml) was simultaneously added to benzene (10 ml) at room temperature. The mixture was stirred for 1 h at room temperature and for 1 h at 60 °C. The organic layer was washed with water and dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The resulting orange oil (272 mg), whose ^1H NMR spectrum showed a peak at δ 1.4, was pyrolyzed (ca. 100—200 °C) in vacuo and di-*t*-butyl selenoketone (79 mg, 38% based on hydrazone used) was collected in a cold trap. (c) Hydrazone **1** (316 mg, 2.02 mmol) in benzene (10 ml) and Se_2Cl_2(555 mg, 2.42 mmol) in benzene (10 ml) was simultaneously added to triethylamine (489 mg, 4.84 mmol) in benzene (20 ml) at room temperature. After water was added, the organic layer was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and then volatile materials were removed completely in vacuo. ^{77}Se NMR spectrum of the residual orange oil showed mainly two comparable peaks at δ 702 and 785. Its elemental analysis was as follows: C, 34.59; H, 6.01; Cl, 9.55; N, 1.09%. These data suggested the composition

$C_9H_{18}ClSe_2$. Calcd for $C_9H_{18}ClSe_2$; C, 33.93; H, 5.69; Cl, 11.13%.

Reactions of 1,1,3,3-Tetramethyl-2-indanselone (3) with Methyllithium. To methyllithium (1.82 mmol) in ether (6 ml) was added the selone **3** (152 mg, 0.606 mmol) in ether (10 ml) at room temperature. The green solution became colorless after 80 min. After stirring for additional 30 min was added aqueous ammonium chloride. The organic layer was separated, washed with water, and dried over anhydrous $MgSO_4$. Removal of the solvent gave an almost colorless oil with characteristic smell of selenol, whose ^1H NMR spectrum showed a peak at δ −0.45 due to a selenol proton. To convert the selenol to the corresponding diselenide the mixture was dissolved in KOH (0.3 g)–MeOH (10 ml) and the solution was stirred at room temperature overnight. Methanol was removed and the residue was extracted with ether. The ethereal layer was washed with water and dried over anhydrous $MgSO_4$ and ether was evaporated. The products were separated by preparative thin-layer chromatography (silica gel, hexane) to give 1,1,3,3-tetramethyl-2-(methylseleno)indan (**8**, R=CH_3) (16 mg, 10%) and bis-(1,1,2,3,3-pentamethyl-2-indanyl) diselenide (**11**, R=CH_3) (118 mg, 73%). **8** (R=CH_3): colorless crystals, mp 54.5—55.0 °C. ^1H NMR δ=1.25 (s, 6H), 1.40 (s, 6H), 2.11 (s, 3H, $SeCH_3$), 3.30 (s, 1H), 7.18 (s, 4H); MS *m/z* (rel intensity) 268 (M^+, 32), 173 (60), 131 (100), 57 (68). Found: *m/z* 268.0722. Calcd for $C_{14}H_{20}{}^{80}Se$: M, 268.0728. **11** (R=CH_3): yellow crystals, mp 143.0—143.5 °C. ^1H NMR δ=1.37 (s, 12H), 1.52 (s, 18H), 7.1—7.2 (m, 8H); ^{13}C NMR δ=25.7, 28.3, 32.6, 50.6, 122.3, 127.0, 148.7; ^{77}Se NMR δ=628; MS *m/z* (rel intensity) 534 (M^+, 0.8), 506 (0.7), 348 (1), 268 (3), 187 (100), 171 (56), 145 (51), 131 (27), 57 (40). Found: C, 62.90; H, 7.11%. Calcd for $C_{28}H_{38}Se_2$: C, 63.15; H, 7.19%.

In a similar manner the following reactions were carried out.

With MeMgI. **3** (72.2 mg, 0.287 mmol) and MeMgI (3.4 equiv) were reacted overnight. **11** (R=CH_3): 53 mg (69%).

With *t*-BuLi. In the case of the reaction of **3** (154 mg, 0.612 mmol) with *t*-BuLi (3 equiv), **3** was not completely consumed even after 3 d. Therefore additional *t*-BuLi (1.5 equiv) was added. *t*-Butyl 1,1,3,3-tetramethyl-2-indanyl selenide (**8**, R=*t*-Bu; 9%): colorless crystals, mp 84.0—84.5 °C. ^1H NMR δ=1.21 (s, 6H), 1.38 (s, 6H), 1.50 (s, 9H, *t*-Bu), 3.04 (s, 1H), 7.19 (s, 4H); ^{13}C NMR δ=28.5, 28.7, 33.7, 38.3, 45.9, 62.8, 122.7, 126.7, 149.70; ^{77}Se NMR δ=325; MS *m/z* (rel intensity) 310 (M^+, 13), 254 (14), 239 (7), 173 (58), 157 (27), 131 (23), 119 (23), 86 (50), 84 (78), 57 (100). Found: *m/z* 310.1214. Calcd for $C_{17}H_{26}{}^{80}Se$: M, 310.1999. Bis(1,1,3,3-tetrametyl-2-indanyl) diselenide (**12**, 66%): yellow crystals, mp 140.5—141.0 °C. ^1H NMR δ=1.25 (s, 12H), 1.48 (s, 12H), 3.69 (s, 2H), 7.19 (s, 8H); ^{13}C NMR δ=28.2, 29.1, 46.9, 74.7, 122.5, 127.0, 149.0; ^{77}Se NMR δ=278; MS *m/z* (rel intensity) 506 (M^+, 0.8), 310 (4), 254 (5), 173 (26), 157 (11), 131 (14), 119 (9), 57 (100). Found: *m/z* 506.1032. Calcd for $C_{26}H_{34}{}^{80}Se_2$: M, 506.0990.

With *t*-BuMgCl. **3** (155 mg, 0.616 mmol) were reacted with *t*-BuMgCl (3 equiv) for 1.25 h. **8** (R=*t*-Bu) (28 mg, 15%), **12** (69 mg, 44%), and 1,1,2,3-tetramethyl-1*H*-indene (**9**) (21 mg, 22%)[17] were obtained.

With $PhCH_2Li$. **3** (107 mg, 0.427 mmol) and $PhCH_2Li$ (3.5 equiv) were reacted for 2 h. 2-Benzyl-1,1,3,3-tetramethyl-2-indanselenol (**7**, R=CH_2Ph; 86%): ^1H NMR δ=−0.5 (s, 1H), 1.5 (s, 6H), 1.6 (s, 6H), 3.3 (s, 2H), 7.0—7.6 (m, 9H); MS *m/z* (rel intensity) 344 (M^+, 2), 263 (20), 247 (12), 171 (8), 157 (8), 91 (65), 74 (64), 59 (100).

With PhLi. **3** (156 mg, 0.620 mmol) was reacted with PhLi (3 equiv) for 30 min. 1,1,3,3-Tetramethyl-2-indanyl phenyl selenide (**8**, R=Ph; 47%): mp 77.0—78.0 °C. ^1H NMR δ=1.31 (s, 6H), 1.32 (s, 6H), 3.49 (s, 1H), 7.1—7.8 (m, 9H); ^{13}C NMR δ=28.5, 28.7, 46.5, 70.9, 122.6, 126.9, 127.1, 129.0, 131.3, 134.2, 149.2; ^{77}Se NMR δ=234; MS *m/z* (rel intensity) 330 (M^+, 24), 173 (100), 158 (11), 131 (75), 99 (8), 91 (29), 85 (14), 71 (17), 57 (61). Found: *m/z* 330.0842. Calcd for $C_{19}H_{22}{}^{80}Se$: M, 330.0884.

With PhMgBr. The reaction of **3** (64 mg, 0.26 mmol) with PhMgBr (2 equiv) was so slow that 1 and 2 equiv. of PhMgBr were added after 7 and 18 h, respectively, and the mixture was warmed at 35 °C for 2 h. **8** (R=Ph) (2.4 mg, 3%) and **9** (6.3 mg, 14%) were obtained.

Preparation of 1,1,3,3-Tetramethyl-2-indanthione (13). **13** was prepared by the reaction of 1,1,3,3-tetramethyl-2-indanone hydrazone (1.04 g, 5.13 mmol) with disulfur dichloride (0.726 g, 5.38 mmol) in benzene.[10] Yield: 0.87 g (83%). Orange crystals; mp 38—43 °C (lit,[7c] 42 °C); ^1H NMR δ=1.47 (s, 12H), 7.31 (s, 4H);[7c] IR (KBr) 1100 cm^{-1}(C=S).

Reactions of 13 with Organolithium Reagents. The reactions were carried out in a similar manner to that described in the reactions of **3** with organometallic reagents.

With MeLi. **13** (102 mg, 0.498 mmol) was reacted with MeLi (3 equiv) for 30 min. 1,1,2,3,3-Pentamethyl-2-indanthiol (**14**, R=CH_3) (100 mg, 91%) was obtained: colorless oil, ^1H NMR δ=1.22 (s, 3H), 1.28 (s, 6H), 1.39 (s, 6H), 7.12—7.20 (br s, 4H); IR (neat) 2585 cm^{-1} (S–H).

With *t*-BuLi. **13** (124 mg, 0.606 mmol) and *t*-BuLi (3 equiv) were reacted for 12 h to give 1,1,3,3-tetramethyl-2-indanethiol (**16**) (40%, 57% based on the consumed thione) and recovered **13** (30%). **16**: mp 33.0—34.5 °C. MS *m/z* (rel intensity) 206 (M^+, 20), 173 (100), 157 (48). Found: *m/z* 206.1136. Calcd for $C_{13}H_{18}S$: M, 206.1129.

With $PhCH_2Li$. **13** (125 mg, 0.610 mmol) and $PhCH_2Li$ (3 equiv) were reacted for 3 h. 2-Benzyl-1,1,3,3-tetramethyl-2-indanethiol (**14**, R=CH_2Ph) (172 mg, 95%): mp 99.0—100.5 °C; ^1H NMR δ=1.1 (s, 1H), 1.4 (s, 6H), 1.6 (s, 6H), 3.1 (s, 2H), 6.9—7.5 (m, 9H); MS *m/z* (rel intensity) 296 (M^+, 2), 262 (45), 247 (52), 232 (8), 204 (23), 171 (67), 157 (21), 91 (100). Found: *m/z* 296.1603. Calcd for $C_{20}H_{24}S$: M, 296.1598.

With PhLi. **13** (165 mg, 0.809 mmol) was reacted with PhLi (3 equiv) for 4 h. 1,1,3,3-Tetramethyl-2-phenyl-2-indanethiol (**14**, R=Ph) (56%) and 1,1,3,3-tetramethyl-2-indanyl phenyl sulfide (**15**, R=Ph) (24%) were obtained. **14** (R=Ph): mp 87.8—89.2 °C; ^1H NMR δ=0.96 (s, 6H), 1.55 (s, 6H), 1.64 (s, 1H), 6.95—7.66 (m, 9H); MS *m/z* (rel intensity) 282 (M^+, 8), 267 (4), 249 (100), 233 (75), 218 (31), 202 (15), 159 (24), 105 (54), 91 (19). Found: *m/z* 282.1437. Calcd for $C_{19}H_{22}S$: M, 282.1442. **15** (R=Ph): ^1H NMR ($CDCl_3$) δ=1.31 (s, 12H), 3.46 (s, 1H), 6.95—7.66 (m, 9H); (C_6D_6) δ=1.27 (s, 6H), 1.36 (s, 6H), 3.49 (s, 1H), 6.87—7.63 (m, 9H).

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