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REACTION OF DIAZOMETHANE WITH SELENOESTERS

PREPARATION OF α-(ALKYL- OR ARYLSELENO)METHYL KETONES AND METHYL KETONES

THOMAS G. BACK* and RUSSELL G. KERR
Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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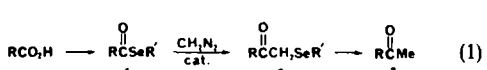
Abstract—The reaction of diazomethane with a series of selenoesters **1** in the presence of CuI, CuSePh or Cu powder produced α-(alkyl- or arylseleno)methyl ketones **2** in yields of 41–65%. Methyl ketones **3** and bis(arylseleno)methanes **9** or **14** were formed as by-products. The direct conversion of selenoesters to methyl ketones was accomplished in high yield by the usual reaction with diazomethane, followed by workup with HBr solution. The simultaneous copper-catalyzed reactions of selenoesters **1c** and **1i** with diazomethane resulted in crossover, with the formation of all four possible α-seleno ketones **2b**, **2c**, **2h** and **2i**. A non-concerted mechanism involving attack by the diazo compound upon the acyl carbon atom of an activated selenoester with the formation of a tetrahedral intermediate **11** has been suggested. The reaction of the selenothiocarbamate **4** with diazomethane resulted in 1,3-dipolar cycloaddition to afford **5** instead of insertion into the acyl–selenium bond.

Diazo compounds undergo insertion reactions into the Se—Se, Se—Cl (or Br), Se—SO_2 and Se—C linkage of diselenides,[1] selenenyl halides,[1c,1d,2] selenosulfonates[3] and allylic[1d,4] or carbonyl-activated[5] selenides, respectively. The majority of these processes occur via either ionic or carbene (or carbenoid) mechanisms (Scheme 1), although a free radical process has been implicated in one case.[3]

We envisaged that the reaction of a selenoester **1** with diazomethane would result in a similar insertion into the acyl–selenium linkage[6] to provide the corresponding synthetically useful α-(alkyl- or arylseleno)methyl ketone **2** via the novel C—C bond-forming reaction shown in Eq. (1).[7] α-Seleno ketones have been previously prepared from, among others, ketones,[8] olefins,[9] acetylenes[10] and phenylselenoacetaldehyde.[11] Since selenoesters are readily available from carboxylic acids[12] as well as from their hydrazides,[13] methyl esters[14] and chlorides,[15] the present approach would provide a versatile source of α-seleno ketones from a variety of carboxylic acid precursors. Furthermore, we sought a convenient *in situ* method for the reductive deselenization of compounds **2** in order to effect the overall transformation of carboxylic acid derivatives to methyl ketones[16] **3** (Eq. 1). We now report our results in this area.



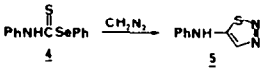
(1)

1 **2** **3**

RESULTS AND DISCUSSION

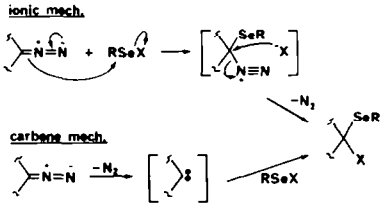
Preparation of α-seleno ketones

Selenoesters were treated with ethereal diazomethane at room temperature in the presence of an appropriate catalyst until TLC or GC indicated the disappearance of the starting material (4–12 hr). The results are summarized in Table 1. Alkyl, aryl, cyclic and heterocyclic selenoesters **1a–1i** afforded the corresponding α-seleno ketones **2a–2i** in yields of 41–65%. Selenocarbonate **1j** furnished a comparable yield of the α-selenoester **2j**, but selenocarbamates **1k** and **1l** provided only poor yields of the corresponding insertion products **2k** and **2l**. The conversion of the unsaturated selenoester **1e** to **2e** proceeded as usual and was not accompanied by the significant formation of cyclopropanated products.[17a] Se-Phenyl N-(phenyl)selenothiocarbamate (**4**) underwent dipolar cycloaddition to the thiocarbonyl group[18] to form the 1,2,3-thiadiazole **5** (Eq. 2) instead of insertion into the C—Se bond.



(2)

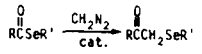
4 **5**



Scheme 1.

The most effective catalysts for the insertion reaction proved to be Cu powder, CuI and CuSePh,[19] with the latter requiring somewhat shorter reaction times. Since these catalysts operate under heterogeneous conditions, we also investigated the use of the soluble phosphite complex $(MeO)_3P \cdot CuI$.[17a,20] This compound caused exceptionally rapid consumption of the starting material in the conversion of **1a** to **2a**, but afforded a poor yield (31%) of the α-seleno ketone and enhanced yields of the usual by-products (*vide infra*, Eq. 3). Other catalysts studied which proved inferior or wholly ineffective were $BF_3 \cdot OEt_2$, $Hg(OAc)_2$, $AgOCOCF_3$, alumina, silica-gel and Zn–Cu couple.[21a] Attempts to perform the insertion reaction by photochemical means (irradiation with a sunlamp) or

Table 1. Preparation of α-seleno ketones



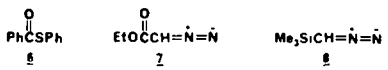
1 2

Selenoester	R	R′	Catalyst[a]	Product	Isolated yield (%)
1a	Ph	Ph	Cu	**2a**	56
			CuSePh		56
1b	Me	Ph	Cu	**2b**	65
			CuI		63
1c	$PhCH_2$	Ph	Cu	**2c**	56
			CuSePh		60
1d		Ph	Cu	**2d**	42
1e		Ph	CuI	**2e**	55
1f	cyclo-C_6H_{11}	Ph	Cu	**2f**	41
			CuSePh		50
1g	Ph	Me	CuI	**2g**	46
1h	$PhCH_2$	*p*-MePh	Cu	**2h**	60
1i	Me	*p*-MePh	Cu	**2i**	62
1j	MeO	Ph	CuI	**2j**	48
			CuSePh		49
1k	PhNH	Ph	Cu	**2k**	19
1l		Ph	Cu	**2l**	16

[a] Reaction times were in the range 4–12 hr, except in the case of **2j**, which required 2 days.

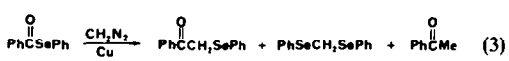
with the Simmons–Smith reagent[21b] were also unsuccessful.

We also examined the possibility of employing thioesters in lieu of selenoesters and diazo compounds other than diazomethane. However, S-phenyl thiobenzoate (**6**) failed to provide the corresponding α-thio ketone when treated with diazomethane under a variety of conditions, and no insertion was observed with selenoesters and either ethyl diazoacetate (**7**) or trimethylsilyldiazomethane (**8**).[22] Evidently thioesters are considerably less reactive than their selenium analogues and the reactivity of diazo compounds is significantly lowered by the presence of the delocalizing ester group in **7** or by the bulky silyl substituent in **8**.



6 **7** **8**

The relatively modest yields of α-seleno ketones **2** in Table 1 prompted us to investigate the by-products. In the transformation of **1a** → **2a**, the product was accompanied by the formation of bis-(phenylseleno)methane (**9**) and acetophenone (**10**), isolated in yields of 29 and 37%, respectively (Eq. 3). Analogous by-products were detected (TLC, NMR), but not always isolated, in the other examples in Table 1.



1a **2a** **9** **10** (3)

Preparation of methyl ketones

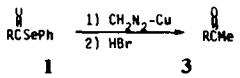
A simple, *in situ* method for converting α-seleno ketones **2** to methyl ketones **3** was also developed. Since the latter compounds are the major by-products of **2** during their preparation from selenoesters **1**(*cf* Eq. 3), it seemed reasonable that the overall conversion of selenoesters (and therefore of other carboxylic acid precursors) to methyl ketones (**1** → **3**) could be accomplished in higher yield than their conversion to α-seleno ketones (**1** → **2**).

We observed that α-seleno ketones **2a** and **2b** were rapidly and quantitatively transformed to the methyl ketones **3a** and **3b**, respectively, upon shaking with concentrated HBr. As expected, the similar treatment of the crude reaction mixtures obtained from selenoesters and diazomethane resulted in the formation of the desired methyl ketones in excellent yield, as shown in Table 2. It is thus possible to efficiently prepare methyl ketones from selenoesters in one step.

Mechanism

Myriad copper-catalyzed reactions of diazo compounds are known and their mechanisms are varied and often unclear.[17a] Although the reaction of selenoesters with diazomethane *formally* comprises an insertion of a CH_2 unit into the acyl–selenium linkage, a simple, concerted insertion of a copper carbenoid intermediate into this bond (path a, Scheme 2) is suspect as it does not readily account for the observed by-products (*cf* Eq. 3). We also considered the possibility that the reaction proceeds via attack by the diazo compound upon the acyl carbon atom with formation

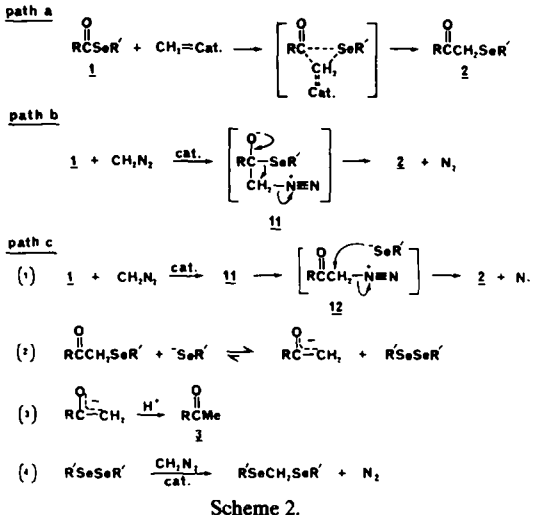
Table 2. Preparation of methyl ketones



1 3

Selenoester	R	Product	Isolated yield (%)
1a	Ph	3a	87
1c	$PhCH_2$	3c	85
1d		3d	78
1e		3e	77
1f	cyclo-C_6H_{11}	3f	75

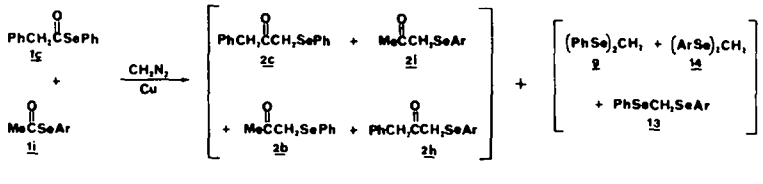
of the tetrahedral intermediate **11**, followed either by rearrangement directly to the product **2** (path b, Scheme 2), or by expulsion of $PhSe^-$ from **11** to form the diazonium ion **12**, and then displacement of nitrogen from **12** by the selenolate (path c, Scheme 2). Path b is similar to the homologation of ketones with diazomethane,[17b] where migration of an alkyl group (instead of PhSe) occurs in an intermediate similar to **11**. Path c on the other hand is reminiscent of the Arndt–Eistert synthesis,[17c] in which an acid chloride undergoes displacement of Cl^- (instead of $PhSe^-$) by diazomethane. Thus, both paths b and c have literature precedents; however, path c has the advantage of providing a simple rationale for the formation of the bis(arylseleno)methane and methyl ketone by-products. The free selenolate generated in path c is expected to react with the product α-seleno ketone, which effectively competes with **12**. The resulting equilibrium (step 2 in path c) is known to strongly favour the diselenide and enolate on the right-hand side,[8b] and since no attempt was made to maintain anhydrous conditions, protonation of the latter species (step 3, path c) accounts for the formation of the methyl ketone. It also appeared reasonable that the remaining by-product, the bis(arylseleno)methane, could arise from the reaction of the diselenide so formed with diazomethane (step 4, path c). Petragnani and Schill[1a] had previously reported that this process occurs photochemically but fails in the dark. However, we have found that in control experiments diphenyl and di-*p*-tolyl diselenides react rapidly and in high yield with diazomethane in the presence of Cu powder to afford the corresponding bis(arylseleno)methanes even in the absence of light. Hence path c provides a satisfactory explanation for all of the observed products from the reaction of selenoesters with diazomethane under the normal conditions. The lower reactivity of ethyl diazoacetate compared to diazomethane is also consistent with this pathway as the intermediate **11** is expected to form more readily from the more nucleophilic diazo compound.



Scheme 2.

We desired to further test the validity of this mechanism. Since only path c invokes the formation of the free selenolate, a crossover experiment was performed to provide corroboration. Thus, equimolar amounts of selenoesters **1c** and **1i** were treated with diazomethane and Cu powder under the usual conditions. These compounds were chosen because their products display sharp, characteristic NMR signals which provide for easy identification. As expected, the normal α-seleno ketones **2c** and **2i** were accompanied by roughly equal amounts of the crossover products **2b** and **2h** (Scheme 3). Furthermore, the unsymmetrical bis(arylseleno)methane **13** was formed along with the bis(phenylseleno) and bis(*p*-tolylseleno) derivatives **9** and **14**. The identity of the products was confirmed by GC–mass spectral analysis. The possibility still remained that the crossover products were generated by the disproportionation of the selenoester precursors prior to their reaction with diazomethane, or by that of the two direct products, α-seleno ketones **2c** and **2i**, subsequent to their formation. Two control experiments were therefore conducted. In one, selenoesters **1c** and **1i** were stirred with Cu powder in the absence of diazomethane and in the other, α-seleno ketones **2c** and **2i** were stirred with Cu powder and diazomethane in the usual manner. Since no significant formation of crossover products (**1b** and **1h** or **2b** and **2h** in the two experiments, respectively) was detected, it can be concluded that crossover occurs during and not before or after the actual reaction of the selenoesters with diazomethane.

These experiments permit us to unequivocally rule out concerted mechanisms such as paths a and b in Scheme 2. They provide strong, but not definitive evidence for path c.



(Ar = p-tolyl)

Scheme 3.

It remains to address the role of the catalyst in this process. For the sake of simplicity, the nucleophile in path c of Scheme 2 is depicted as free diazomethane. However, it is well known[17d] that diazo compounds form complexes with various metals and the formation of such a complex may precede attack upon the selenoester. Moreover, selenoesters are relatively inert toward nucleophiles unless first activated. This can be achieved through the presence of certain soft metal cations which presumably coordinate with the Se atom, thereby increasing the positive character of the adjacent acyl C atom and so rendering it more susceptible to nucleophilic attack. It has recently been reported that the acylating power of selenoesters is significantly enhanced by Cu(I)[23] and Cu(II)[14] species. That Cu powder is capable of a similar role was easily confirmed by comparing the rate of methanolysis of selenoester **1a** in the presence and absence of this catalyst. Whereas the control solution failed to react significantly after 48 hr at room temperature, the one containing Cu powder produced 43% of methyl benzoate after a similar period.[24] It therefore appears that all of the catalysts successfully employed in this work are capable of activating the selenoester toward attack by nucleophiles, and thus, in the case of diazomethane, facilitating the formation of the intermediate **11**.

It is interesting to consider one other possibility. If it is assumed that both selenoesters and diazo compounds are capable of coordinating with Cu species, then perhaps it is also possible that simultaneous coordination of both reactants occurs, thereby lowering the activation energy of the transition state leading to **11**. Further work is needed, however, to permit a clear understanding of the function of the catalyst in this reaction.

EXPERIMENTAL

M.ps were obtained on an A. H. Thomas hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer 467 spectrometer. NMR spectra were obtained on a Hitachi Perkin–Elmer R24B or a Varian XL-200 spectrometer. All NMR spectra were obtained in $CDCl_3$ solution and are reported in ppm downfield from TMS. Mass spectra and GC–mass spectra were recorded on a Varian MAT CH5 and on a Hewlett–Packard 5990A instrument, respectively. GC analyses were performed on a Varian 3700 chromatograph equipped with a Varian CDS 111 integrator. Stainless steel columns (2 m) packed with 3% OV-17 on Chromosorb W-HP were employed for both GC and GC–mass spectral determinations. Preparative TLC was carried out on Analtech 20 × 20 cm glass plates coated with silica-gel GF (1000 μm).

Ethereal alcohol-free diazomethane was prepared from N-methyl-N-nitroso-*p*-toluenesulfonamide ("Diazald", Aldrich Chemical Co.) by a standard method.[25] All experiments with diazomethane were conducted in a fume hood behind a safety shield. Copper powder and cuprous iodide (ultrapure grade) were obtained from the Baker and Adamson Div. of the Allied Chemical Co., and from the Alfa Chemical Co., respectively. The CuSePh was prepared by a previously described procedure.[19] All other reagents were purchased from commercial sources.

Preparation of selenoesters

Selenoesters **1a–1f** and selenocarbonate **1j** were prepared from the oxidation of the corresponding hydrazides with benzeneseleninic acid in the presence of triphenylphosphine as reported previously.[13] Selenoester **1g** was obtained by the method of Kozikowski and Ames.[14]

Se-*p-Tolyl* 2-(*phenyl*)*selenoacetate* (**1h**). Selenoester **1h** was obtained in 62% yield by the same procedure as **1e**,[13] except that *p*-toluenseleninic acid[26] was employed instead of benzeneseleninic acid. The product had m.p. 43° (CH_2Cl_2–hexane); IR (film, melt) 1705 cm^{-1}; NMR δ 7.1–6.6 (complex, 9H), 3.48 (s, 2H), 2.01 (s, 3H); mass spectrum, *m/e* (relative intensity, %) 290 (M^+, ^{80}Se, 6), 288 (M^+, ^{78}Se, 4). (Found: C, 61.91; H, 4.92. Calc for $C_{15}H_{14}OSe$: C, 62.28; H, 4.89%.)

Se-*p-Tolyl selenoacetate* (**1i**). Selenoester **1i** was prepared in 55% yield from acethydrazide and *p*-toluenseleninic acid by the same general procedure as **1b**.[13] The product was an oil; IR (film) 1725 cm^{-1}; NMR δ 7.21 (d, J = 9 Hz, 2H), 7.01 (d, J = 9 Hz, 2H), 2.26 (s, 3H), 2.21 (s, 3H); mass spectrum, *m/e* (relative intensity, %) 214 (M^+, ^{80}Se, 12), 212 (M^+, ^{78}Se, 5). (Found: C, 50.42; H, 4.79. Calc for $C_9H_{10}OSe$: C, 50.71; H, 4.74%.)

Se-*Phenyl* N-(*phenyl*)*selenocarbamate* (**1k**). Diphenyl diselenide (1.56 g, 5.0 mmol) was added to a soln of $NaBH_4$ (0.38 g, 10.0 mmol) and NaOH (0.40 g, 10.0 mmol) in 10 ml of water and 15 ml of EtOH.[27] The mixture was refluxed until a clear soln was obtained (*ca* 10 min). The soln was cooled to 0° and acidified with HCl aq. Phenyl isocyanate (1.0 g, 8.4 mmol) was added dropwise and the resulting white ppt was filtered and washed with 3 × 5 ml of hexane to afford 2.25 g (97%) of crude **1k**, m.p. 121–125° (from CH_2Cl_2–hexane); IR ($CHCl_3$) 3400, 1690 cm^{-1}; NMR 7.6–6.6 (complex); mass spectrum, *m/e* (relative intensity, %) 157 ($PhSe^+$, ^{80}Se, 35), 119 ($PhNCO^{+\cdot}$, 67). (Found: C, 56.47; H, 4.03; N, 4.81. Calc for $C_{13}H_{11}NOSe$: C, 56.53; H, 4.02; N, 5.07%.)

Se-*Phenyl* N,N'-(*diphenyl*)*selenoallophanate* (**1l**). Diphenyl diselenide (1.56 g, 5.0 mmol) was reduced as in the previous procedure, except that the acidification step was omitted. After cooling to 0°, phenyl isocyanate (1.0 g, 8.4 mmol) was added and the soln was stirred for 2 hr. The mixture was diluted to 50 ml with water, extracted with 3 × 50 ml of CH_2Cl_2, dried with anhyd $MgSO_4$ and concentrated *in vacuo*. Chromatography over 25 g of silica-gel afforded 0.32 g of diphenyl diselenide (eluant hexane) and 1.50 g (45%) of the title compound (eluant hexane–benzene, 50:50), m.p. 182° (from dichloromethane–hexane); IR (KBr) 3270, 3250, 1726, 1663 cm^{-1}; NMR δ 7.6–7.1 (complex); mass spectrum, *m/e* (relative intensity, %) 157 ($PhSe^+$, 17), 119 ($PhNCO^{+\cdot}$, 61). (Found: C, 60.16; H, 4.11; N, 6.81. Calc for $C_{20}H_{16}N_2O_2Se$: C, 60.76; H, 4.09; N, 7.09%.)

Se-*Phenyl* N-(*phenyl*)*selenothiocarbamate* (**4**). The procedure was identical to that for **1k**, except that phenyl isothiocyanate was employed instead of phenyl isocyanate. The crude product was formed quantitatively; recrystallization from dichloromethane–hexane gave m.p. 102–104°; IR ($CHCl_3$) 3340, 1600, 1497, 1442, 1370, 950, 698 cm^{-1}; NMR δ 8.0 (broad s, 1H), 7.7–6.8 (complex, 10H); mass spectrum, *m/e* (relative intensity, %) 293 (M^+, ^{80}Se, 3), 291 (M^+, ^{78}Se, 2). (Found: C, 53.09; H, 3.68; N, 4.86; S, 10.75. Calc for $C_{13}H_{11}NSSe$: C, 53.42; H, 3.80; N, 4.79; S, 10.97%.)

Preparation of α-(alkyl- or arylseleno)methyl ketones, esters and carbamates **2a–2l** (Table 1)

All of the title compounds were prepared in the same manner as in the typical case of **2a** (below), from *ca* 100–200 mg of the corresponding selenoesters **1a–1l** and the appropriate catalyst. The products were separated by preparative TLC; by-products were not always isolated. Spectral and physical properties of the products are provided below.

Typical procedure: α-(*phenylseleno*)*acetophenone* (**2a**). Selenoester **1a** (100 mg, 0.38 mmol) and Cu powder (50 mg) were stirred with excess ethereal diazomethane. Additional portions of the diazo compound were added periodically to maintain the reagent in excess at all times. After 6 hr, TLC indicated no remaining starting material. The mixture was filtered, concentrated and separated by preparative TLC in benzene to afford the following components: (a) bis(phenylseleno)methane, 18 mg (29% based on total available selenium), R_f 0.90, identical to an authentic sample,[14] (b) α-seleno ketone **2a**, 59 mg (56%), R_f 0.52, with IR,

NMR and mass spectra in accord with the literature,[11] and (c) acetophenone, 17 mg (37%), R_f 0.18, identical to an authentic sample.

α-(Phenylseleno)acetone (**2b**). R_f 0.27 (benzene); IR, NMR and mass spectra were as reported in the literature.[11]

1-Phenyl-3-(phenylseleno)propanone (**2c**).[9d] R_f 0.42 (benzene), oil; IR ($CHCl_3$) 1700 cm^{-1}; NMR δ 7.6–6.9 (complex, 10H), 3.76 (s, 2H), 3.52 (s, 2H); mass spectrum, *m/e* (relative intensity, %) 290 (M^+, ^{80}Se, 14), 288 (M^+, ^{78}Se, 7).

2-[α-(Phenylseleno)acetyl]thiophene (**2d**). R_f 0.42 (benzene), m.p. 45–46° (from CH_2Cl_2–hexane); IR ($CHCl_3$) 1655 cm^{-1}; NMR δ 7.6–6.8 (complex, 8H), 3.94 (s, 3H); mass spectrum, *m/e* (relative intensity, %) 282 (M^+, ^{80}Se, 16), 280 (M^+, ^{78}Se, 8). (Found: C, 51.18; H, 3.48. Calc for $C_{12}H_{10}OSSe$: C, 51.24; H, 3.59%.)

1-Phenylseleno-11-dodecen-2-one (**2e**). R_f 0.38 (25% benzene–hexane), m.p. 37–39° (from hexane); IR (Nujol) 1695, 1635 cm^{-1}; NMR δ 7.5–7.0 (complex, 5H), 5.9–5.3 (m, 1H), 5.0–4.6 (m, 2H), 3.45 (s, 2H), 2.6–1.0 (complex, 16H); mass spectrum, *m/e* (relative intensity, %) 338 (M^+, ^{80}Se, 37), 336 (M^+, ^{78}Se, 17). (Found: C, 63.80; H, 7.97. Calc for $C_{16}H_{26}OSe$: C, 64.07; H, 7.78%.)

α-(Phenylseleno)acetylcyclohexane (**2f**). R_f 0.41 (benzene), oil; identified by comparison with literature spectra.[11]

α-(Methylseleno)acetophenone (**2g**). R_f 0.58 (20% EtOAc–hexane), oil; IR ($CHCl_3$) 1670 cm^{-1}; NMR δ 8.0–7.1 (complex, 5H), 3.65 (s, 2H), 1.99 (s, 3H); mass spectrum, *m/e* (relative intensity, %) 214 (M^+, ^{80}Se, 26), 212 (M^+, ^{78}Se, 13). (Found: C, 51.04; H, 4.92. Calc for $C_9H_{10}OSe$: C, 50.71; H, 4.74%.)

1-Phenyl-3-(p-tolylseleno)propanone (**2h**). R_f 0.49 (benzene), m.p. 37° (from CH_2Cl_2–hexane); IR (film) 1700 cm^{-1}; NMR (200 MHz) δ 7.4–7.1 (complex, 5H), 3.85 (s, 2H), 3.55 (s, 2H), 2.33 (s, 3H); mass spectrum, *m/e* (relative intensity, %) 304 (M^+, ^{80}Se, 19), 302 (M^+, ^{78}Se, 9). (Found: C, 63.68; H, 5.04. Calc for $C_{16}H_{16}OSe$: C, 63.36; H, 5.33%.)

α-(p-Tolylseleno)acetone (**2i**). R_f 0.52 (benzene), oil; IR (film) 1700 cm^{-1}; NMR (200 MHz) δ 7.42 (d, J = 8 Hz, 2H), 7.09 (d, J = 8 Hz, 2H), 3.53 (s, 2H), 2.32 (s, 3H), 2.25 (s, 3H); mass spectrum, *m/e* (relative intensity, %) 228 (M^+, ^{80}Se, 77), 226 (M^+, ^{78}Se, 57). (Found: C, 53.18; H, 5.11. Calc for $C_{10}H_{12}OSe$: C, 52.87; H, 5.33%.)

Methyl α-(phenylseleno)acetate (**2j**).[28] R_f 0.43 (benzene), oil; IR ($CHCl_3$) 1731 cm^{-1}; NMR δ 7.5–6.8 (complex, 5H), 3.48 (s, 3H), 3.33 (s, 2H); mass spectrum, *m/e* (relative intensity, %) 230 (M^+, ^{80}Se, 100), 228 (M^+, ^{78}Se, 69).

N-Phenyl-α-(phenylseleno)acetamide (**2k**). R_f 0.43 (20% ethyl acetate–hexane), m.p. 67–68° (from CH_2Cl_2–hexane); IR (film, melt) 3300, 1659 cm^{-1}; NMR δ 7.82 (broad s, 1H), 7.5–6.8 (complex, 10H), 3.40 (s, 2H); mass spectrum, *m/e* (relative intensity, %) 291 (M^+, ^{80}Se, 10), 289 (M^+, ^{78}Se, 6). (Found: C, 57.46; H, 4.44; N, 4.59. Calc for $C_{14}H_{13}NOSe$: C, 57.93; H, 4.52; N, 4.83%.)

N,N'-Diphenyl-N-(phenylselenoacetyl)urea (**2l**). R_f 0.72 (30% ethylacetate–hexane), m.p. 76–78° (from CH_2Cl_2–hexane); IR ($CHCl_3$) 3425, 3340, 1686, 1678 cm^{-1}; NMR δ 7.85 (broad s, 1H), 7.5–6.8 (complex, 15H), 3.46 (s, 2H); mass spectrum, *m/e* (relative intensity, %) 291 ($PhNHCOCH_2SePh^+$, ^{80}Se, 27), 289 ($PhNHCOCH_2SePh^+$, ^{78}Se, 14). (Found: C, 61.29; H, 4.53; N, 6.76. Calc for $C_{21}H_{18}N_2O_2Se$: C, 61.61; H, 4.44; N, 6.84%.)

Reaction of selenothiocarbamate **4** *with diazomethane*

Compound **4** (200 mg, 0.68 mmol) was stirred for 2 hr with excess ethereal diazomethane. The concentrated soln was separated by preparative TLC (20% EtOAc–hexane) to afford 60 mg (50%) of **5**, R_f 0.10, with physical and spectral properties as reported in the lit.[29]

Preparation of methyl ketones (Table 2)

All of the compounds in Table 2 were prepared in the same manner as the typical example **3a**. All of the products have been previously reported[30,31] and were identified by their IR and NMR spectra.

Typical procedure: acetophenone (**3a**). Selenoester **1a** (150 mg, 0.57 mmol) and Cu powder (50 mg) were stirred with excess ethereal diazomethane as in the preparation of **2a**. When the reaction was complete, the mixture was filtered and the filtrate was shaken with 5 ml of 48% HBr soln for *ca* 2 min. The aqueous layer was removed, the soln was washed with water, dried over $MgSO_4$, concentrated *in vacuo*, and separated by preparative TLC (benzene) to afford 60 mg (87%) of acetophenone, R_f 0.40, identical to an authentic sample.

Bis(phenylseleno)methane (**9**)[1a]

Diphenyl diselenide (50 mg, 0.16 mmol), Cu powder (50 mg) and excess ethereal diazomethane were stirred in a vessel completely wrapped in aluminum foil to exclude light. After 4 hr, the mixture was filtered and the filtrate was purified by preparative TLC (10% benzene–hexane) to afford 50 mg (96%) of the title compound, R_f 0.75; NMR δ 7.6–7.2 (complex, 10H), 4.22 (s, 2H); mass spectrum, *m/e* (relative intensity, %) 328 (M^+, $^{80}Se_2$, 13), 326 (M^+, ^{80}Se—^{78}Se, 12), 324 (M^+, $^{78}Se_2$, 7).

Bis(p-tolylseleno)methane (**14**)[32]

The title compound was prepared by the same method as **9** in 92% yield, R_f 0.78 (10% benzene–hexane); NMR δ 7.43 (d, J = 7 Hz, 4H), 7.09 (d, J = 7 Hz, 4H), 4.15 (s, 2H), 2.32 (s, 6H); mass spectrum, *m/e* (relative intensity, %) 356 (M^+, $^{80}Se_2$, 26), 354 (M^+, ^{80}Se—^{78}Se, 24), 352 (M^+, $^{78}Se_2$, 15).

Crossover experiment

A mixture of selenoester **1c** (138 mg, 0.50 mmol), selenoester **1i** (107 mg, 0.50 mmol) and Cu powder (50 mg) was stirred with excess ethereal diazomethane for 8 hr. The catalyst was filtered and the filtrate was evaporated *in vacuo*. The 200 MHz NMR spectrum of the resulting oil contained all of the signals observed from superimposing the individual spectra of **2b**, **2c**, **2h** and **2i** (the close proximity of some of these peaks prevented accurate integration, but the products appear to be present in roughly equal amounts), as well as three signals at δ 4.21, 4.18 and 4.14 attributed to the three bis(arylseleno)methanes **9**, **13** and **14**, in the ratio of 1 : 1.9 : 1.1. GC–mass spectral analysis (temperature program: 1 min at 150°, 10° per min to 250°, 30 min at 250°) indicated fully separated components with retention times of 4.9, 6.0 and 12.8 min, identified as **2b**, **2i** and **2c**, respectively, followed by partly overlapping peaks for **2h**, **9**, **13** and **14**.

In a separate experiment, a mixture of α-seleno ketones **2c** (44 mg) and **2i** (50 mg) were treated with Cu powder and ethereal diazomethane under the usual conditions for 6 hr. No significant amounts of new products were observed (GC, NMR). Similarly, no reaction was observed when selenoesters **1c** (50 mg) and **1i** (50 mg) were stirred with Cu powder in ether for a similar length of time.

Methanolysis of Se*-phenyl selenobenzoate* (**1a**)

The selenoester (50 mg) and Cu powder (20 mg) were stirred for 48 hr in 3 ml of MeOH. At this time GC analysis revealed the presence of both **1a** and methyl benzoate in the ratio of 57 : 43. The identity of the latter compound was confirmed by IR, NMR and GC–mass spectra. When the experiment was repeated in the absence of Cu powder, no significant amount of methyl benzoate was detected.

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