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SELONES AS INTERMEDIATES IN THE PREPARATION OF EXTREMELY STERICALLY HINDERED MOLECULES

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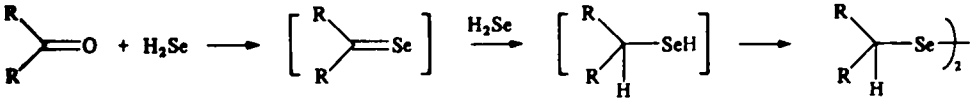
Abstract—The preparation and reactions of selones, selenium analogues of ketones, are described with particular emphasis on their utility in the preparation of extremely sterically hindered molecules. Mechanistic questions related to these reactions are discussed and evidence for "active selenium" is presented. Selenophilic additions of organometallic compounds to selones are also reported.

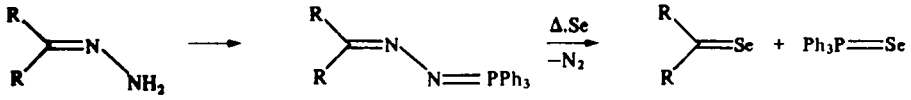
INTRODUCTION

The chemistry of selones, selenium analogues of ketones, has only recently been investigated. Early reports of the preparation of selones by the reaction of hydrogen selenide with ketones, analogous to the synthesis of thiones using hydrogen sulfide, were subsequently shown to be inaccurate, leading instead to diselenides (**2**) by reduction of the intermediate selone (**1**) to the selenol, followed by oxidative dimerization.[1]



1 **2**

The first preparation of a true selone, was reported by Back *et al.*[2] This synthesis involved conversion of a sterically hindered hydrazone (**3**) to its phosphoranylidene hydrazone derivative (**4**) via triphenylphosphine dibromide. Pyrolysis at approx. 180° of the phosphoranylidene hydrazone in the presence of excess selenium led to moderate to good yields of the selones.



3 **4**

The very existence of selones unstabilized by resonance or ligands was in fact considered surprising. The poor overlap properties of the 2p–3p π bond of thiones were assumed to account for the lowered stability and high reactivity of these compounds relative to ketones.[3] The selone 2p–4p π bond should be significantly less stable than the π bond of a thione for the same reasons. As yet no detailed calculations have been reported on the nature of bonding in a pure selenocarbonyl bond which could account for the remarkable stability of selones, however it is likely that the extreme steric hindrance of the selones as yet prepared prevents many intermolecular routes of decomposition, leading to this stability.

There has been considerable speculation about the nature of the "pure" C=Se double bond. Are selones in fact true analogues of ketones? What is the polarization of the selenocarbonyl moiety?

Recent calculations based on ^{77}Se and ^{17}O NMR data on selones and ketones show that the bond order of the selenocarbonyl and carbonyl groups are remarkably similar.[4] Selones also show $n \rightarrow \pi^*$ transitions paralleling those of thiones and ketones.[5] This evidence is consistent with double bond character in a pure selenocarbonyl bond.

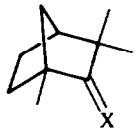
The polarity of the C=Se double bond of the selone deserves special comment. Some calculations [6,7] and dipole moment[8] studies of thiones suggest a "reversed polarity" of these compounds relative to ketones where the thiocarbonyl carbon is slightly negative relative to sulfur. This reversed polarity was initially used to explain thiophilic additions of organometallic reagents to thiones (*vide infra*).[9,10] Presumably selones should show an even greater tendency toward "reversed polarity". Orbital electronegativity calculations[11] do not support this suggestion (Table 1).

In each case, carbon is $\delta+$ relative to the chalcogen for both the σ and π components of the carbonyl, thiocarbonyl and selenocarbonyl moieties. Prelimi-

Table 1. Orbital electronegativities in carbonyl, thiocarbonyl and selenocarbonyl compounds, Pauling scale[11]

	C	O	S	Se
σ sp^2	2.75	5.54	3.46	3.29
πp	1.68	3.19	2.40	2.31

nary dipole moment measurements (fenchone 2.99D, thiofenchone 2.75D, selenofenchone 2.68D)[12] are consistent with a diminished, but not reversed, polarity of these bonds.



X = O, S, Se

The phosphoranylidene hydrazone (*vide supra*) route proved to be extremely useful in the preparation of sterically hindered selones (Table 2). Less sterically hindered phosphoranylidene hydrazones such as derivatives of camphor or benzophenone led only to olefins via an *in situ* twofold extrusion reaction (*vide infra*).[2] Derivatives of easily enolizable ketones led only to complex mixtures of uncharacterized products. The mechanism of this selone forming reaction has been unclear and will be discussed below.

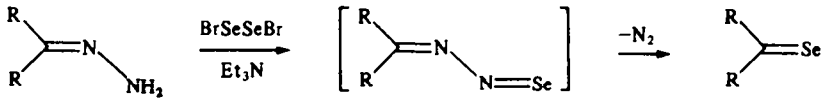
A convenient alternative to the phosphoranylidene hydrazone route to selones has recently been independently reported by two groups. The method involves the reaction of selenium(I) bromide with a hydrazone[13] (or selenium(I) chloride with a hydrazone dimagnesium salt[14]) in the presence of a tertiary amine. It appears as if the reaction proceeds via a N-selenonitrimine (**5**) intermediate which then extrudes nitrogen affording the selone. Again, only very sterically hindered selones could be prepared using this method. No selones were obtained from camphor, benzophenone or fluorenone hydrazones.[13]

A third method has been reported which utilizes bistricyclohexyltin selenide–boron trichloride (**6**) for the preparation of selenofenchone.[15] Presumably this reaction involves *in situ* generation of a low molecular weight form of boron selenide as a selenating reagent. Phosphorus(V) selenide does not react with ketones or thiones to form selones.[13] The insolubility of phosphorus(V) selenide has to date prevented the preparation of selenating reagents such as the selenium analogue (**7a**)[13] of the widely used sulfurating agent *p*-methoxyphenylthioxophosphine sulfide dimer (**7b**).[16] The preparations of selones are summarized in Table 2.

Selones are typically deep blue materials, stable for prolonged periods at 150° under an inert atmosphere.[2] No reaction occurs in visible light as long as oxygen is excluded. Selones are quantitatively reduced with sodium borohydride to the unstable selenols (**8**) which are easily oxidized in air to the diselenides (**9**). Oxidation of the selone with peracids leads to the corresponding ketone (**11**), presumably through a selenine (**10**) intermediate. Heating a selone with excess sulfur leads to selenium extrusion and formation of the corresponding thione (**12**).[17] Attempted protonation of selones in superacid media led only to polymeric materials, in contrast to the corresponding thiones which afforded stable protonated ions.[18]

Selones prove to be efficient radical traps, reacting with a variety of transient radicals affording persistent selenoalkyl radicals. Selones are more reactive in these additions than the corresponding thiones.[19,20] The photochemistry of selones has also been described.[21,22]

Perhaps the most useful applications of selones in organic synthesis have been in the preparation of extremely sterically hindered molecules via cycloadditions. Back *et al.* first utilized selones in investigations



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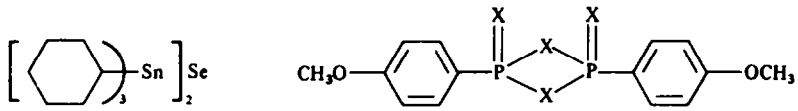
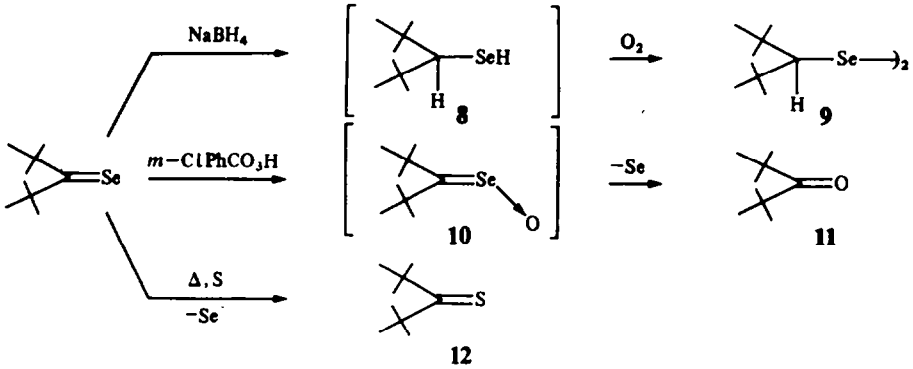
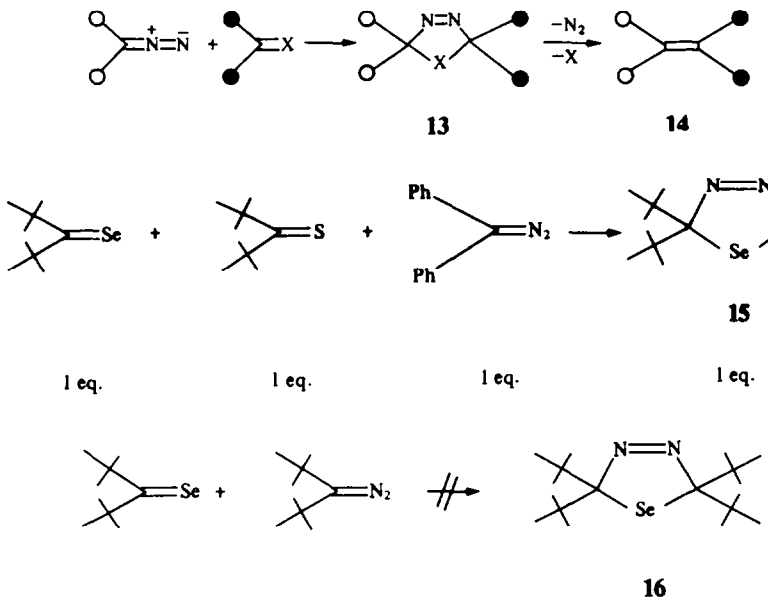


6 **7a** X = Se
7b X = S



8 **9** **10** **11** **12**



of twofold extrusion reactions for the preparation of extremely sterically hindered olefins.[2] This approach involves the preparation of a sterically hindered thia- or selenadiazoline (**13**) via a cycloaddition of a diazo compound with a thione or a selone. In this way, the bulky groups are kept as far apart as possible in the intermolecular reaction. In the less sterically demanding intramolecular reaction nitrogen is thermally extruded affording an episulfide or episelenide which is convertible to the olefin (**14**).

In the twofold extrusion reaction the diazo compound can be prepared separately and often the intermediate selenadiazoline can be isolated.[2] Alternatively the phosphoranylidene hydrazone can be used as an *in situ* source of diazo compound,[2] or as an *in situ* source of both diazo compound and selone[23] (Scheme 1).

In these reactions selones proved to be far more reactive than the corresponding thiones. In a competition reaction, an equimolar mixture of di-t-butyl selone and the corresponding thione were treated with an equivalent of diphenyldiazomethane. Only selenadiazoline (**15**) could be detected.[2] In some twofold extrusion reactions selone additions were successful where the corresponding thione additions failed.[24] An additional advantage in using selones in twofold extrusions is that the intermediate episelenides are thermally unstable, directly extruding selenium and affording the corresponding olefin; episulfides are typically thermally stable compounds which require the use of tertiary phosphines at elevated temperatures for desulfurization.[25]

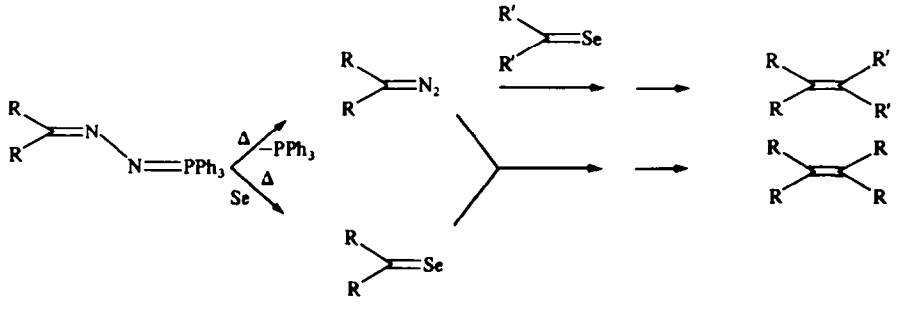
Twofold extrusion reactions of diazo compounds with selones have led to a variety of extremely hindered olefins (Table 3). There are however some limitations to this method. Reaction of the extremely hindered di-t-butyldiazomethane with di-t-butyl selone does not give the intermediate selenadiazoline (**16**);[2] apparently extreme steric interactions prevent its formation.

In some cases retrocyclizations of the selenadiazolines predominate.[2,26] In the attempted preparation of di-t-butylmethylene fenchane (**18**), the only olefin obtained was bifenchylidene (**19**).[2] Presumably the desired selenadiazoline (**17**) forms, but retrocyclizes rather than extrudes nitrogen. The resulting diazofenchane reacts normally with the selone forming bifenchylidene (Scheme 2).

Even when the extremely hindered unsymmetrical selenadiazoline (**20**) was isolated, no unsymmetrical olefin (**21**) could be obtained upon thermolysis.[27] Extremely high pressures (15 kbar) did not change the course of the retrocyclization. Such retrocyclizations are especially prevalent when the selenadiazoline substituents differ markedly in size (e.g. **17**, **20**).

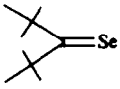
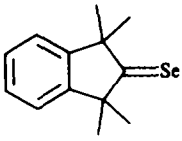
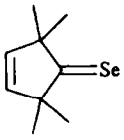
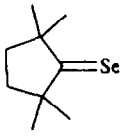
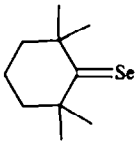
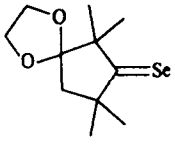
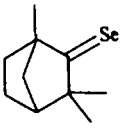
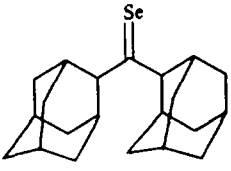
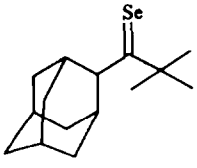
Photolysis of selenadiazolines provides a convenient route to sterically hindered unsymmetrical and symmetrical azines (**22**).[27]

A related twofold extrusion reaction of selones with



Scheme 1.

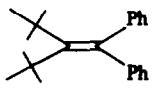
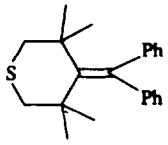
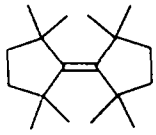
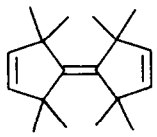
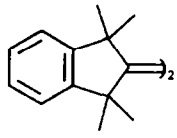
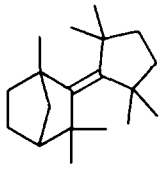
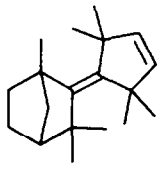
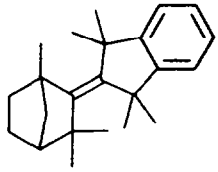
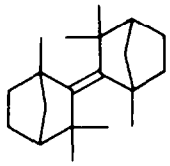
Table 2. Preparation of selones, isolated yields based on hydrazone

Selone	Method[a]	Yield	Ref.
	A	29 (75)	2 (19)
	B	65	13
	A	75	37
	B	80	13
	A	53	23
	B	70	13
	A	54	13
	B	68	13
	A	40	13
	B	73	13
	A	48	13
	B	80	13
	A	25	2
	B	76	13
	D	90[b]	15
	C	53	14
	C	43	14

[a] A, phosphoranylidene hydrazone; B, selenium(I) bromide; C, selenium(I) chloride; D, bis-tricyclohexyltin selenide.

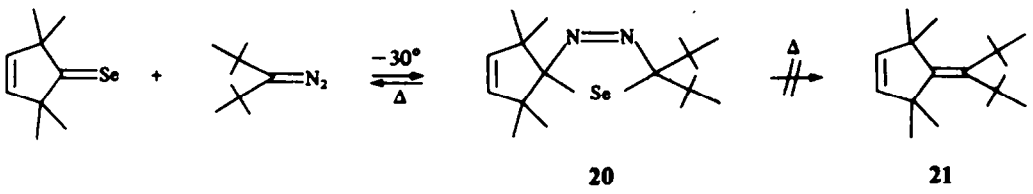
[b] Yield based on ketone.

Table 3. Olefin synthesis via twofold extrusion reactions of selones

Olefin	Method[a]	Isolated yield	Ref.
	A	49	2
	A	72	26
	A	70	27
	A	31	
	B	65	23
	C	65	
	B	65	37
	A	30	27
	A	42	27
	A	20	27
	B	24[b]	2

[a] A, selone-diazo compound; B, selone-phosphoranylidene hydrazone; C, selenium-phosphoranylidene hydrazone.

[b] Single isomer.



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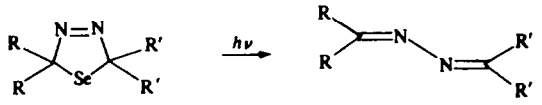
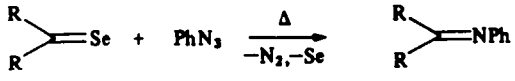


22

aromatic azides proved useful for the preparation of extremely sterically hindered anils (23).[28] In this reaction selones again proved to be more reactive than thiones, and afforded purer products.



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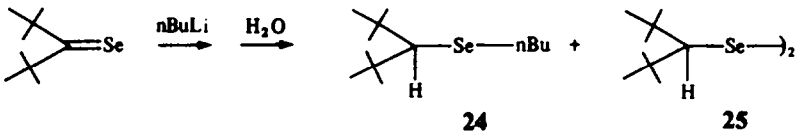
RESULTS AND DISCUSSION

While selones have proved to be extremely useful in the preparation of sterically hindered molecules, much of the mechanistic chemistry associated with the preparation and reactions of selones remains unclear. Recently we have investigated some of these aspects of selone chemistry.

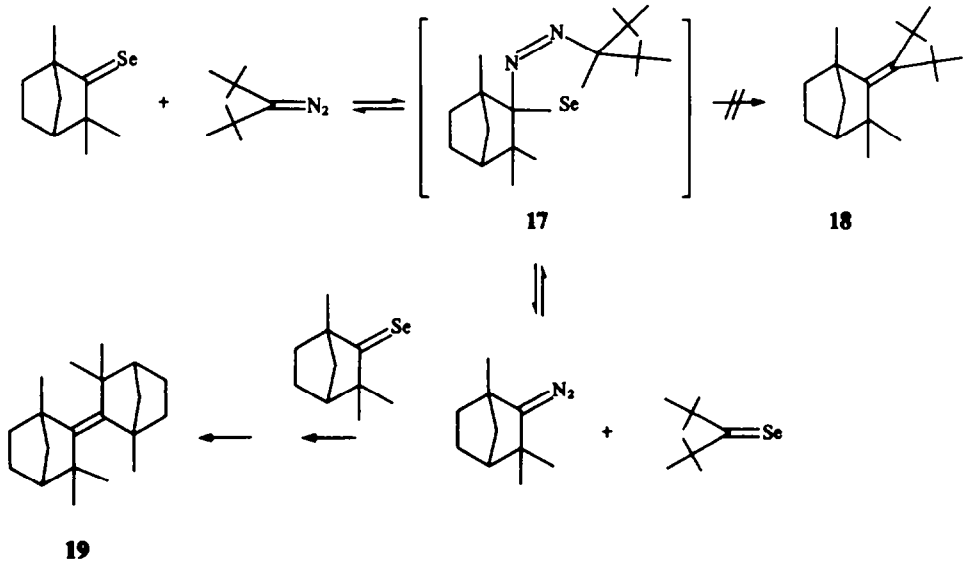
The reactions of thiones with organometallic reagents are known in many cases to give significant addition of the organometallic to the S atom of the thiocarbonyl bond—thiophilic addition.[9,10] In general, mixtures of sulfides and thiols are obtained via reactions at the sulfur and carbon centers of the thiones. Radical anion intermediates have been implicated in the reactions of aliphatic thiones with alkyl lithium reagents.[29]

The lower polarity and greater bond length of the selenocarbonyl bond as well as the ability of selenium to stabilize an α-radical prompted us to investigate the reactions of selones with organometallic reagents.

Di-t-butyl selone reacts with n-butyl lithium to give predominately the selenide (24) by selenophilic addition. Small amounts of reduction product isolated as the diselenide (25) also were observed. Surprisingly, no product resulting from reaction at carbon (or the derived diselenide) could be detected from the reaction. Similarly only the selenophilic addition product could



24 25



17 18 19

Scheme 2.

be obtained from the reaction of the same selone with phenyl lithium.

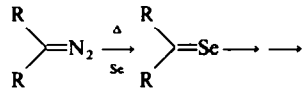
Selenophilic addition yields remain essentially invariant under conditions of temperature and solvent where the corresponding reactions of thiones lead to predominant reaction at carbon. The mechanistic details of selenophilic additions are currently under investigation.

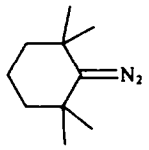
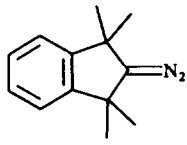
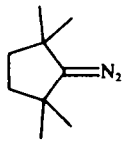
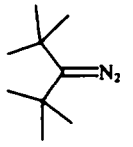
The mechanistic course of the phosphoranylidene hydrazone reaction was also intriguing. In this reaction selone formation does not occur below the temperature at which the phosphoranylidene hydrazone thermally cleaves to form triphenylphosphine and diazo compound. Small amounts of diazo compound are usually observed in the initial stage of the selone-forming reaction by such a cleavage. Dimeric olefins are often significant by-products in the selone preparations in cases where an *in situ* twofold extrusion reaction is possible. We were interested in determining whether the diazo compound could be an intermediate in selone formation.

Diazo-2,2,6,6-tetramethylcyclohexane (**26**), 2-diazo-1,1,3,3-tetramethylindane (**27**), diazo-2,2,5,5-tetramethylcyclopentane (**28**) and di-t-butyl diazomethane (**29**) were treated with metallic (gray) selenium powder for 2 hr at 175°, a typical temperature for phosphoranylidene hydrazone pyrolysis. The cyclohexane derivative (**26**) gave no detectable selone (or selone-derived products). The indane derivative (**27**) gave approx. 2% olefin, the expected product when selone is generated in the presence of excess diazo compound. The cyclopentane derivative (**28**) gave a mixture of selone, selenadiazoline and olefin which would indicate approx. 10% selone formation. Di-t-butyl diazomethane (**29**) afforded di-t-butyl selone in 34% yield. Symmetrical azines were also isolated in the last three cases: (**27**) 28%, (**28**) 18% and (**29**) 16% yield.

The half-lives of diazo compounds (**26–29**) were then determined spectroscopically in refluxing n-octane (126°) (Fig. 1). These half-lives were 9, 10, 22 and 68 min, respectively. Apparently there is a definite relationship between diazo compound half-life and yield of selone, with greater stability leading to increased selone formation (Table 4). This still leaves unexplained the

Table 4. Thermal reactions of sterically hindered diazo compounds



Diazo compound		Yield[a] of selone formed (%)	$t_{1/2}$ Diazo compound (126°)
26		—	9 min
27		2	10 min
28		10	22 min
29		34	68 min

[a] Includes selone, selenodiazoline and olefin.

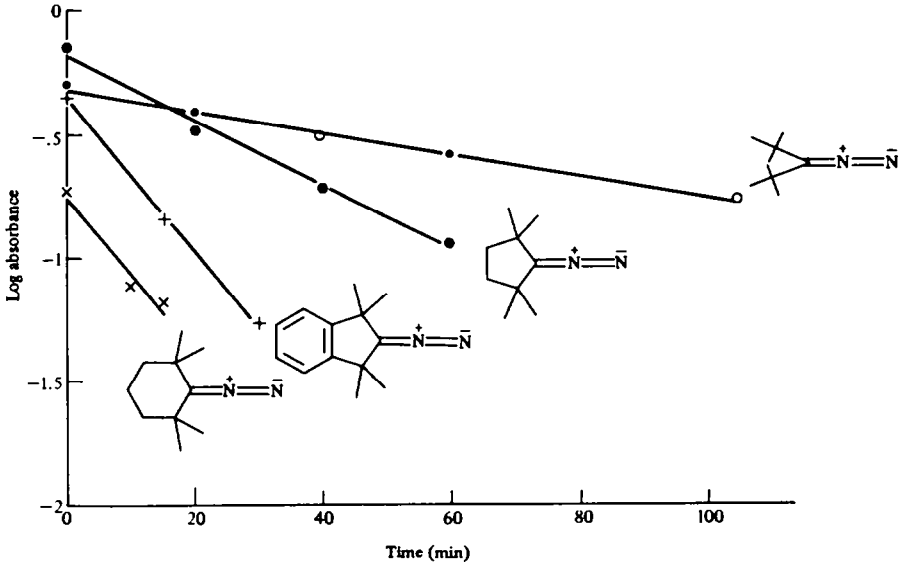
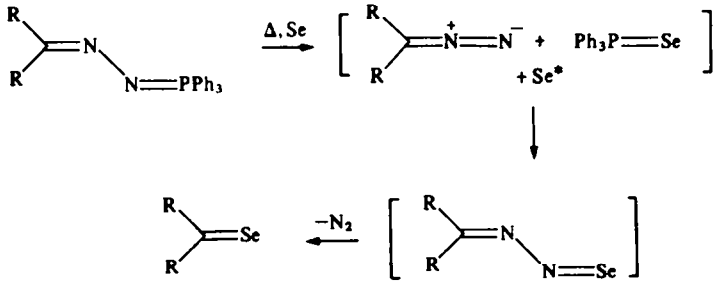


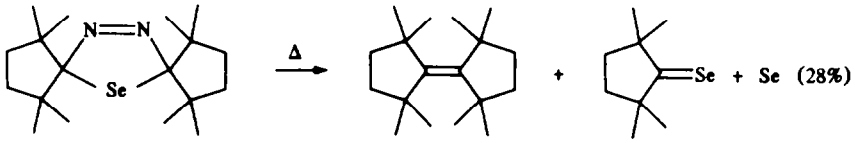
Fig. 1. Diazo compound thermolysis in octane (126°).



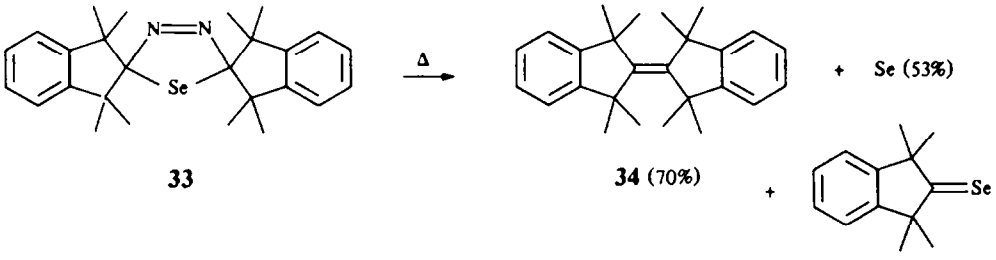
reason for significantly greater yields of selones from pyrolysis of the phosphoranylidene hydrazones in the presence of selenium than in the direct reaction of diazo compound with selenium if diazo compounds are in fact intermediates in this reaction. A possible reason might be based on the structure of elemental selenium.

Elemental selenium exists as either Se_8 rings or Se_n chains (*n* approx. 10,000).[30] Above 110° selenium exists primarily in the Se_n state. These structures contain very few termini which typically exist as selenium radicals. These termini would be expected to be the most reactive sites in selenium aggregates. One can envision the small probability of a diazo compound encountering one of the few reactive termini increasing with increasing thermal stability of the diazo compound, paralleling the observed yields of selone.

selenium behaving quite differently from selenium aggregates in selone reactions. Pyrolysis of isolated selenadiazolines typically affords, aside from the desired olefin, small amounts of retrocyclization products (selones and diazo compounds), azines and products of diazo compound decomposition. During the course of the study of pyrolyses of selenadiazolines (**30** and **33**) it was noted that **30** afforded olefin (**31**) in 68% yield and selone (**32**) in 44% yield—an apparent impossibility since we had presumed that the selone could only arise from retrocyclization of selenadiazoline (a maximum of 32%). Similarly selenadiazoline (**33**) afforded olefin (**34**) in 70% yield plus selone (**35**) in 43% yield. In each case the recovered selenium, 28 and 53%, respectively, was significantly less than that expected from the observed extrusion.[33]



30 **31** (68%) **32** (44%)



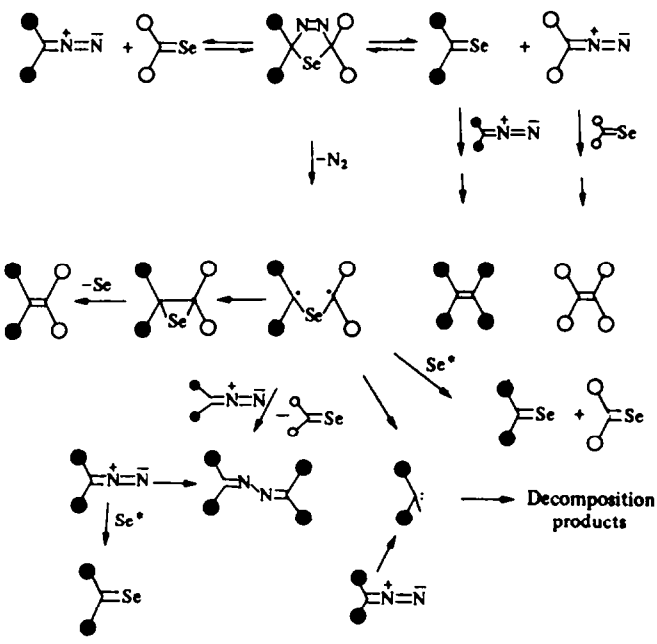
33 **34** (70%) **35** (43%)

The by-product from thermal reactions of phosphoranylidene hydrazones affording diazo compounds is triphenylphosphine. The triphenylphosphine generated in the thermal reaction also reacts with selenium affording triphenylphosphine selenide.[2] Considering the high affinity of triphenylphosphine for selenium,[31] the possibility for reaction at non-terminal selenium atoms is quite good.[32] A reaction at an internal site on the selenium chain would sever the chain creating two new termini. If the process was to occur immediately after phosphoranylidene hydrazone cleavage the newly thermally liberated (reactive) diazo compound would be in the immediate vicinity of a selenium terminus. This proximity effect may be critical since added triphenylphosphine does not increase selone yields in direct reaction of selenium with diazo compounds.

There is additional evidence for a "reactive form" of

Apparently selones must be formed efficiently from diazo compounds in the extrusion reactions. It is unlikely that carbenes or carbenoid compounds are intermediates since in no case have we been able to trap unrearranged products in intermolecular reactions. More likely, a reactive, low molecular weight species of selenium[32] generated in the extrusion reaction reacts with diazo compound (or possibly the selenocarbonyl ylide) to afford the additional selone. While the site of the reaction of diazo compounds with the "active" selenium is questionable, it is possible that an N-selenonitrosimine (**5**), similar to that implicated in the selenium(I) halide reaction is the reactive intermediate. The possible courses of twofold extrusion reactions are indicated in Scheme 3.

Especially reactive forms of sulfur formed in similar extrusions have been previously reported.[34] While it



Scheme 3. Possible courses of selone twofold extrusion reactions.

would be tempting to suggest that atomic selenium is the active reagent in these reactions, we have no reason at this time to postulate anything more than a non-aggregated selenium species.

EXPERIMENTAL

General methods

Sterically hindered ketones are most easily prepared by the methods of Rathke and Millard[35] or Klages and Voss.[36] Others have been previously described.[2,23,37,38] Tetrahydrofuran was distilled from benzophenone–sodium, triethylamine was distilled from barium oxide and diethylene glycol was distilled before use. Organic solutions were dried over sodium sulfate, and solvents were removed under reduced pressure on a rotary evaporator. ^{1}H- and ^{13}C-NMR spectra were obtained with JEOLCO PS 100 and Varian XL 200 spectrometers using TMS as an internal reference. IR and UV-visible spectra were recorded on Perkin–Elmer 382 and 320 spectrophotometers. Mass spectra were obtained on a Hewlett–Packard 5995A GC–MS. Melting points are uncorrected. Satisfactory elemental analysis or exact mass determination were obtained for all new compounds.

1,1,3,3-*Tetramethyl-2-indanone hydrazone*[37]

1,1,3,3-Tetramethyl-2-indanone[38] (18 g, 96 mmol) and excess hydrazine hydrate (25 ml) in diethylene glycol (35 ml) were stirred and heated to reflux for 4 days. The mixture was cooled, added to water (50 ml) and extracted with ether (4 × 50 ml). The combined organic layers were washed with water, saturated brine and dried. Evaporation of solvent gave colorless crystals of the hydrazone. Two crops of colorless needles were obtained from hexanes (15.1 g, 78%), m.p. 106–106.5°; IR ($CHCl_3$) 3540, 1682, 1640, 1510, 1482, 1478, 1390, 1335 cm^{-1}; ^{1}H-NMR (CCl_4) δ 7.18 (s, 4H), 5.2 (bs, 2H), 1.60 (s, 6H), 1.35 (s, 6H).

1,1,3,3 - *Tetramethyl* - 2 - *indanone triphenyl* - *phosphoranylidenehydrazone*[37]

Bromine (24.6 g, 154 mmol) in dry benzene (180 ml) was added over 30 min to a stirred, ice cooled soln of triphenylphosphine (37.4 g, 144 mmol) in dry benzene (440 ml). After an additional 30 min of stirring, 1,1,3,3-tetramethyl-2-indanone hydrazone (30.2 g, 149 mmol) and Et_3N (44 ml, 32.4 g, 320 mmol) in dry benzene (160 ml) were added over a period of 1 hr. After 5 hr at room temp the mixture was filtered and concentrated to give yellow crystals. Recrystallization from chloroform–hexanes gave the phosphazine (61.2 g, 89%) as three crops of yellow needles: m.p. 165°; IR (CCl_4) 3070, 1490, 1258, 1118, 1030 cm^{-1}; ^{1}H-NMR (CCl_4) δ 8.0–7.3 (complex, 15H), 7.15 (s, 4H), 1.82 (s, 6H), 1.20 (s, 6H).

2 - *Diazo* 1,1,3,3-*tetramethylindane* (27)

(a) 1,1,3,3-Tetramethyl-2-indanone hydrazone (0.22 g, 1.1 mmol), barium manganate[39] (700 mg) and calcium oxide (700 mg) in CH_2Cl_2 (4 ml) were stirred for 2 hr at room temp. The mixture was filtered through Celite, concentrated via a rotary evaporator and purified by Kugelrohr distillation at 50° (0.5 Torr) to give pure diazo compound (0.180 g, 82%) as red crystals, m.p. 67°; IR (film) 2030, 1480, 1380, 1360, 750 cm^{-1}; UV (cyclohexane) λ_{max} 257 nm (ε = 9700), 502 nm (ε = 5); ^{1}H-NMR (CCl_4) δ 7.13 (m, 4H), 1.50 (s, 12H).

(b) The phosphoranylidene hydrazone (8.0 g, 173 mmol) was heated in an oil bath at 195° while volatiles were distilled at 1 Torr into a dry ice–acetone trap until no more diazo compound was produced. Kugelrohr distillation afforded material identical to that obtained in (a) in 20% yield.

1,1,3,3-*Tetramethylindane-2-selone* (35)[13,37]

(a) Phosphoranylidene hydrazone (20 g, 43 mmol) and excess Se powder (12 g) were heated at 185° (1 Torr) while volatiles were distilled into a dry ice–acetone trap affording a blue oil which contained the selone, small amounts of diazo compound and rearrangement products. Bulb-to-bulb distillation gave pure selone (9.5 g, 88%) as dark blue crystals, m.p. 40–43°; IR (melt) 1590, 1485, 1455, 1355, 1050, 755 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.32 (s, 4H), 1.51 (s, 12H); ^{13}C-NMR ($CDCl_3$) δ 294.0, 147.4, 127.7, 123.4, 67.3, 31.3; MS, *m/e* 252 M^+ (^{80}Se).

(b) The hydrazone (1.0 g, 5 mmol) in CH_2Cl_2 (15 ml) and selenium(I) bromide (1.6 g, 5 mmol) in CH_2Cl_2 (15 ml) were simultaneously added dropwise over 15 min to a cooled 0° soln of freshly distilled Et_3N (1.1 g, 11 mmol) in CH_2Cl_2 (20 ml). The mixture was then allowed to come to room temp and

stirred for 30 min. The resulting suspension was filtered, the filtrate was washed with water and quickly filtered through a layer (approx. 4.0 g) of K_2CO_3 and dried. The CH_2Cl_2 was removed under reduced pressure on a rotary evaporator below room temp. The residue was carefully heated (50–75°) with a heat gun under reduced pressure (approx. 0.5 Torr) while the volatile selone collected in a dry ice–acetone-cooled receiver. (In this step stirring the distilling flask facilitates distillation of the selone.) Deep blue selone identical to that described in (a) was obtained in 80% yield.

Bi-1,1,3,3,-tetramethyl-2-indanylidene (**34**)

(a) 1,1,3,3-Tetramethylindane-2-selone (4.50 g, 18 mmol) and the indanone phosphoranylidene hydrazone (8.25 g, 18 mmol) were heated to 185° under argon with stirring. After 5 days, CH_2Cl_2 (10 ml) was added to the cooled mixture. Filtration gave white crystals which upon recrystallization from $CHCl_3$–MeOH afforded the pure olefin (4.0 g, 65%) as colorless plates, m.p. 255°; IR (KBr) 1600, 1490, 1450, 1380, 1360, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.15 (bs, 8H), 1.77 (s, 24H); ^{13}C-NMR ($CDCl_3$) δ 154.4, 151.0, 126.6, 121.9, 50.3, 33.1; MS, *m/e* 344 (M^+).

(b) To a stirred soln of selone (146 mg, 0.58 mmol) in 2 ml THF was added dropwise 2-diazo-1,1,3,3-tetramethylindane (116 mg, 0.58 mmol). Solvent removal afforded 261 mg of a white crystalline material. This intermediate selenadiazoline was heated under N_2 for 24 hr at 190°. Upon cooling the residue was dissolved in hot $CHCl_3$ and filtered. Solvent removal and recrystallisation of the residue from $CHCl_3$–MeOH afforded pure olefin (141 mg, 71%) identical to that obtained in part (a).

N-(1,1,3,3-*Tetramethyl-2-indanylidene*) *aniline* (**23**)

Tetramethylindanselone (550 mg, 2.2 mmol) and phenyl azide (390 mg, 3.3 mmol) were heated to reflux in benzene (5 ml) under N_2 for 14 hr. After removal of solvent the residue was sublimed with a Kugelrohr distillation apparatus at 60° (0.6 Torr) to give 290 mg, 50% yield of pure, white crystalline anil, m.p. 119.5–122°; ^{1}H-NMR ($CDCl_3$) δ 1.40 (d, 12H); 7.40–6.76 (complex m, 9H); 7.30 (s, 4H); ^{13}C-NMR ($CDCl_3$) δ 187.5, 150.0, 148.0, 147.0, 122.8–122.5, 122.3, 118.9, 49.4–48.0, 29.8–29.4 ppm; MS, *m/e* 263 (M^+); IR (film): 1683, 1599, 1360, 1310, 1220, 1040, 700, 670 cm^{-1}.

1,1,3,3-*Tetramethyl-2-indanyl phenyl selenide*

To **35** (251 mg, 1 mmol) in dry THF (5 ml) under positive argon pressure was added dropwise a phenyl lithium soln (1 mmol, 1.8 M in 3:1 benzene–ether) over approx 8 min. Immediate decolorization of the selone occurred. Water (5 ml) was added and the mixture extracted with ether (3 × 5 ml). The combined organic layers were dried and concentrated. Column chromatography (silica–hexanes) afforded the selenide as a yellow oil in 47% yield, b.p. (Kugelrohr oven temp) 107° (3.5 Torr); ^{1}H-NMR ($CDCl_3$) δ 1.34–1.33 (broad s, 12H); 3.48 (s, 1H); 7.80–7.14 (m, 9H); MS, *m/e* 330 (M^+) (^{80}Se); IR (neat) 1580, 1480, 1460, 1450, 1440, 1380, 1365, 1310, 1060, 1020, 865, 755, 735, 700, 690 cm^{-1}.

Bis - 1,1,3,3 - tetramethylindane - 2 - spiro - 2',5' - Δ^3 - 1',3',4' - selenadiazoline (**33**)

Compound **27** (0.4 g, 2 mmol) was slowly added with stirring to a soln of **35** (0.5 g, 2 mmol) in anhyd THF (2 ml). The blue color of the selone was slowly discharged during the course of the reaction and when equimolar amounts of each reagent were present, the soln became colorless and the selenadiazoline precipitated out of soln. Solvent removal with a stream of N_2 followed by drying at 0.1 Torr afforded yellow crystals of the selenadiazoline (0.89 g, 99%). Recrystallization from THF gave light yellow crystals, m.p. 170°; IR (KBr) 1590, 1580, 1485, 1450, 1380, 1365, 1310, 976, 855 cm^{-1}; UV (cyclohexane) λ_{max} 306 nm (ε 750); ^{1}H-NMR ($CDCl_3$) δ 7.15 (s, 8H), 1.48 (s, 12H), 1.16 (s, 12H); ^{13}C-NMR ($CDCl_3$) δ 148.4, 131.3, 127.4, 122.6, 52.8, 34.3, 24.4.

Diazo-2,2,6,6-tetramethylcyclohexane (**26**)

2,2,6,6-Tetramethylcyclohexanone hydrazone[13] (300 mg, 1.79 mmol), barium manganate[39] (700 mg, 1.87 mmol), calcium oxide (700 mg) and sand[40] (1 g) in CCl_4 (3 ml) were stirred for 2 hr. Filtration through celite, solvent removal and Kugelrohr distillation (50°, 0.5 Torr) gave pure diazo compound as an orange oil (250 mg, 83%); IR (neat) 2030, 1470, 1385, 1370 cm^{-1}; ^{1}H-NMR (CCl_4) δ 1.46 (m, 6H), 1.14 (s, 12 H).

Diazo-2,2,5,5-tetramethylcyclopentane (**28**)

(a) 2,2,5,5-Tetramethylcyclopentanone hydrazone[41] (300 mg, 1.9 mmol), barium manganate[39] (800 mg, 2.1 mmol), calcium oxide (800 mg), and sand (1 g) in CH_2Cl_2 (3 ml) were vigorously stirred for 2 hr. Filtration through celite, solvent removal and Kugelrohr distillation (40°, 0.5 Torr) gave pure diazo compound (150 mg, 50%) as a red oil; IR (neat) 2030, 1460, 1385, 1365, 1255 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.64 (s, 4H), 1.21 (s, 12H).

(b) 2,2,5,5-Tetramethylcyclopentane triphenylphosphoranylidene hydrazone[41] (10.1 g, 24.4 mmol) was heated at 175°, with stirring, while volatiles were collected in a dry ice–acetone trap at 0.5 Torr. The total yield of red diazo compound collected was (1.5 g, 40%) which was identical with that obtained in part (a).

Thermolysis of di-t-butyldiazomethane (**29**) *in octane*

General procedure. Di-t-butyldiazomethane[2] was dissolved in octane (5 ml), a visible spectrum (488 nm) was obtained and then the soln was heated to reflux by immersing into an oil bath which had been preheated to 175°. After 20 min the flask was removed and immersed into a room temp water bath. After 5 more min of cooling another spectrum was obtained. Similarly after reheating, spectra were obtained after 40, 60 and 105 min. The data showed a half-life of 68 min.

Diazo-2,2,6,6-tetramethylcyclohexane (**26**). Thermolysis following the general procedure with visible spectra (480 nm) taken at 0, 10 and 15 min indicated a half-life of 10 min.

2-Diazo-1,1,3,3-tetramethylindane (**27**). Thermolysis following the general procedure with visible spectra (502 nm) taken at 0, 15 and 30 min indicated a half-life of 10 min.

Diazo-2,2,5,5-tetramethylcyclopentane (**28**). Thermolysis following the general procedure with visible spectra (509 nm) taken at 0, 20, 40 and 60 min indicated a half-life of 22 min.

Reaction of diazoalkanes with selenium powder

General procedure. The diazo compound (approx. 100 mg) and Se powder (approx. 300 mg) were heated at 175°, with stirring under N_2 in a flask fitted with an air cooled condenser. After 2 hr the residue was taken up in pentane ($CHCl_3$ was used for **27**) and filtered through celite. Solvent removal gave a residue which was weighed. The residue was taken up in deuterochloroform and the product distribution was determined by ^{1}H-NMR and GC.

Di-t-butyldiazomethane (**29**). Pyrolysis of di-t-butyldiazomethane[2] (95 mg, 0.62 mmol) following the general procedure led to the recovery of a residue which weighed 57 mg, which was shown to be a mixture containing azine (16% yield) and di-t-butyl selone (34% yield).

Diazo-2,2,6,6-tetramethylcyclohexane (**26**). Pyrolysis following the general procedure, of diazo compound (180 mg, 1.1 mmol) gave only volatile decomposition products and no observed 2,2,6,6-tetramethylcyclohexane selone.

2-Diazo-1,1,3,3-tetramethylindane (**27**). Pyrolysis following the general procedure, of diazo compound (100 mg, 0.5 mmol) afforded azine (25 mg, 28%) and a trace (2%) of **34**.

Diazo-2,2,5,5-tetramethylcyclopentane (**28**). Pyrolysis of diazo compound (83 mg, 0.55 mmol) following the general procedure led to recovery of a residue weighing 30 mg which was shown to be a mixture of azine (18% yield), **33** (7% yield), **23** (12% yield) and **35** (0.4% overall yield).

Bis - 2,2,5,5 - tetramethylcyclopentane - spiro - 2'5'-Δ^3-1',3',4' - selenadiazoline (**30**)

Preparation from selone[13] and **28** gave this selenadiazoline in 97% yield. Recrystallization from THF gave an analytical sample, m.p. 126–127°; IR (KBr) 1585, 1460, 1382, 1365, 1250, 980, 860 cm^{-1}; UV (cyclohexane) λ_{max} 302 nm (ε 745); ^{1}H-NMR ($CDCl_3$) δ 2.26–1.68 (complex, 8H), 1.16 (s, 12H), 0.81 (s, 12H); ^{13}C-NMR ($CDCl_3$) δ 127.99, 46.6, 39.2, 32.0, 26.2.

Pyrolysis of bis - 1,1,3,3 - tetramethylindane - 2 - spiro - 2',5' - Δ^3 - 1',3',4' - selenadiazoline (**33**)

Compound **30** (261 mg, 0.58 mmol) was heated under argon at 164° for 4 hr then at 170° for 12 hr, and finally at 190° for 12 hr. The selone (**31**) which was present was collected by distillation (0.5 Torr, 50°) affording 65 mg, 43% yield. The residue was dissolved in hot $CHCl_3$ and filtered affording Se powder (24 mg, 53%) and a soln containing **32** (0.41 g, 70%). All recovered compounds were identical to authentic samples (GC, NMR).

Pyrolysis of bis-2,2,5,5 - tetramethylcyclopentane - spiro - 2',5' - Δ^3 - 1',3',4' - selenadiazoline (**30**)

Selenadiazoline (**30**) (243 mg, 0.68 mmol) was heated under argon at 165° for 4 hr, then at 170° for 12 hr, and finally at 190° for 12 hr. The selone (**32**) which was present was collected by distillation (0.5 Torr, 45°) affording 62 mg, 44% yield. The residue was dissolved in chloroform and filtered giving Se powder (14.9 mg, 28%) and a soln containing **31** (116 mg, 68%). All recovered compounds were identical to authentic samples (GC, NMR).

Reaction of di-t-butyldiazomethane (**29**) *with selenium powder and triphenylphosphine*

Di-t-butyldiazomethane[2] (90 mg, 0.58 mmol), Se powder (300 mg) and triphenylphosphine (150 mg, 0.57 mmol) were heated at 175° with stirring, under N_2, in a flask fitted with an air cooled condenser. After 2 hr the residue was taken up in pentane and filtered through celite. Solvent removal and Kugelrohr distillation (50°, 0.5 Torr) gave di-t-butylselone (35 mg, 0.17 mmol, 29%). Similarly no enhanced yield of selone was observed upon reactions with diazo compounds (**26–28**).

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