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A Convenient and High Yielding Procedure for the Preparation of Isoselenocyanates. Synthesis and Reactivity of O-Alkylselenocarbamates.

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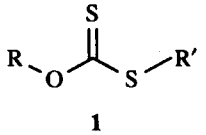
Abstract: A high yielding one pot procedure for the preparation of isoselenocyanate from the corresponding formamide is reported. Various aromatic and aliphatic primary amines were employed in order to prepare the isoselenocyanates to establish the generality of the procedure. *O*-Alkylselenocarbamates of various primary, secondary and tertiary alcohols were synthesized and their stability and comparative reactivity were studied. Radical deoxygenation of the selenocarbamate of a secondary and a tertiary alcohol was accomplished under various conditions.

Today, the chalcogeno derivatives of alcohols constitute a very important class of compound, due to their proven usefulness in radical deoxygenation[1] and also in the Chugaev olefination.[2] Over the years, a variety of chalcogeno derivatives have been employed in a plethora of applications.[1,2] These derivatives include, xanthates[1,2] **1**, thionoimidazolides[1,2] **2**, thionobenzoates[3] **3**, selenocarbonates[4] **4**, etc. The thionocarbamates **5** on the other hand, do not offer any 'free radical' chemistry,[5] though they are a well known class of compounds.[6a] A lot of patented information exists on the use of this class of compounds in the agricultural industry.[6b-d] The lack of reactivity of thionocarbamates in radical reactions is attributed to the reduced radicophilicity of the C=S bond, as the lone pair of electrons of the nitrogen is delocalized over the carbon-sulfur double bond.[1a] It was conceived that the selenocarbamates **6**, should offer the desired reactivity in the radical deoxygenation reactions as the selenium is more radicophilic. Interestingly, selenocarbamates have not been properly studied, and little is known about the chemistry of this class of compounds.[7]



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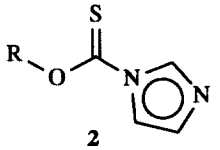

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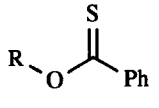

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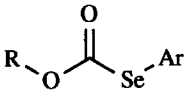

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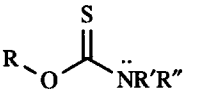

R′ and R″= alkyl

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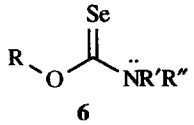

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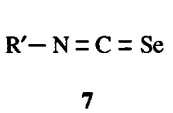

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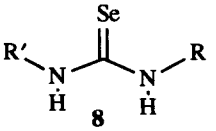

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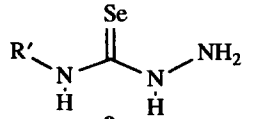

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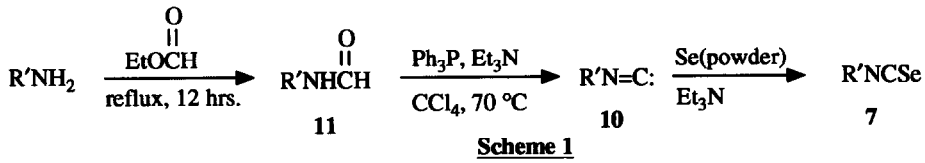
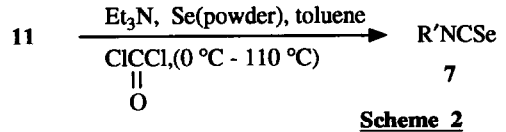
In order to have easy accessibility to various *O*-alkylselenocarbamates **6**, we needed to have a general method to prepare the requisite isoselenocyanates **7**. Besides, both the aliphatic and aromatic isoselenocyanates are important precursors for a number of other organoselenium compounds such as selenoureas **8** and selenosemicarbazides **9**.[8] The literature to date contains few descriptions of the preparation of isoselenocyanates.[7a,9-14] The classical method of synthesis of organic isoselenocyanates involves the addition of elemental selenium to isonitriles **10**.[9] Several other methods have also been investigated. A seemingly more convenient procedure consists of treatment of a primary amine, together with equimolar amounts of CSe_2 and $HgCl_2$ in the presence of triethylamine giving the corresponding isoselenocyanate in reasonable yields.[10] The disadvantages of this method are that the presence of isoselenocyanate and the amine-mercuric chloride adduct leads to the formation of the corresponding selenourea and carbodiimide (R-N=C=N-R) as major side products, which makes the purification of the desired material difficult.[10] Moreover, carbon diselenide is notorious for its objectionable odor. These reasons make the method not suitable for our needs and for any large scale preparation. Other methods of only limited applicability include, the alkylation of selenocyanate ion[11], the reaction of *N*-arylcarbimidic dichlorides with sodium selenide[12], the treatment of isocyanates with phosphorous(V) selenide[12b], and photochemical rearrangement of selenocyanates.[13] Only the first classical method has proved feasible for general use.[14] However, the preparation and subsequent handling of the noxious isonitriles as starting material may not be a desirable method of choice.

We wish to report here a new one-pot procedure for the preparation of isoselenocyanates **7** from the corresponding formamides **11**. The formamides of primary amines are either commercially available or can be readily prepared in excellent yields, as shown in Scheme 1. Upon treatment of various formamides **11 a-h**, with phosgene (employed as solution in toluene) in the presence of excess selenium black (powder) and triethylamine, the corresponding isoselenocyanates **7a-f** were obtained in good overall yields as shown in Scheme 2. Appel and Ziehn had reported[15] a general and convenient procedure for making isonitriles. We prepared various isonitriles using their procedure. Then, we did comparison studies to demonstrate that the yields of this *in-situ* preparation are better than the conventional method (treatment of isonitrile and selenium powder) in some cases and comparable in others (Table 1), Furthermore, handling of the noxious isonitriles can be easily avoided in our method, as the isonitrile would be immediately consumed upon generation. We did not adapt the procedure of Appel and Ziehn instead for the one pot preparation of isoselenocyanate, because addition of elemental selenium in the presence of Ph_3P would result in the formation of $Ph_3P(Se)$. It is noteworthy however, that we were also unable to use this method to make both the *p*-nitrophenyl and pentafluorophenyl derivatives, as they gave several unidentifiable products. Similar observations were made by Appel and Ziehn as well.[15] We believe that the reason for this anomaly is the reduced nucleophicity and high reactivity of the isonitrile, which could have led to polymerization. Even employing *t*-butyltetramethyl

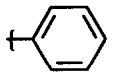
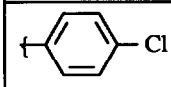
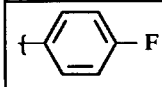
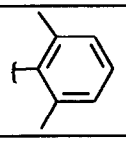
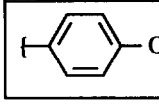


Scheme 1



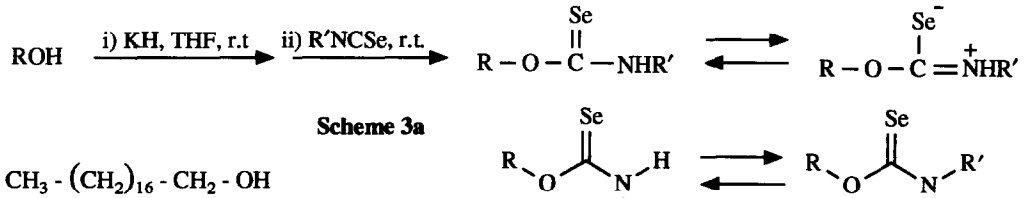
Scheme 2

Table 1

R'=	R'NHCHO (Yields %)	R'NC (Yields %) Scheme 1	R'NCSe (Yields %) Scheme 1	Overall Yield R'NHCHO → R'NCSe Scheme 1	Scheme 2
	**11a** (Commercial)	**10a** (Commercial)	**7a** (89)	(69)	(78)
	**11b** (Commercial)	**10b** (88)	**7b** (85)	(75)	(79)
	**11c** (93)	**10c** (78)	**7c** (45)	(33)	(65)
	**11d** (96)	**10d** (88)	**7d** (70)	(59)	(63)
	**11e** (93)	**10e** na	**7e** na	na	(68)
	**11f** (95)	**10f** (91)	**7f** (79)	(69)	(50)

guanidine instead of triethylamine did not make any difference.

Selenocarbamates of simple alcohols have been prepared before, as they have found use as chelating agents to prepare organometallic complexes.[7c] Jensen and coworkers prepared the first *N*-unsubstituted selenocarbamates.[7b] Sonoda has reported preparation of *N*-cyclohexyl selenocarbamates of simple alcohols in 49% yield, by heating the corresponding isoselenocyanate in the presence of large excess of alcohol.[7a] This method is of course unsuitable for general use. Having at hand a convenient procedure of making the isoselenocyanates, we synthesized the corresponding *O*-alkylselenocarbamates



Scheme 3a

Scheme 3b

12 14 15 13 16

Table 2

alcohol \ isoselenocyanate	7a	7b	7c	7d	7e	7f
	selenocarbamate[a] (yields %)					
12	**6a** (60)	na	na	na	na	na
13	**6b** (74)	**6c** (82)	**6d** (88)	**6e** (91)	**6f** (69)	**6g** (89)
14	**6h** (80)	**6i** (65)	**6j** (87)	**6k** (70)	**6l** (67)	na
15	**6m** (92)	**6n** (88)	na	na	na	na
16	**6o** (78)	na	na	na	**6p** (90)	na

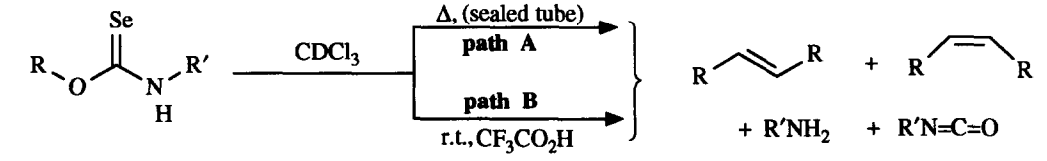
[a] The selenocarbamates have been numbered in the sequence they appear, e.g. reaction of the alcohol **12** with the isoselenocyanate **7a** gave **6a** etc.

6a-p of various alcohols, e.g. octadecanol **12**, cyclododecanol **13**, cholestanol **14**, diacetone glucose **15**, and cedrol **16**, as depicted in the Scheme 3a. Deprotonation of the alcohols with potassium hydride worked better than NaH or BuLi in terms of overall yields. Thus, in a typical preparation, a THF solution of isoselenocyanate was added to the potassium salt of an alcohol in THF at room temperature and the reaction was followed by tlc for the disappearance of the starting material. The yields of various selenocarbamates synthesized are reported in Table 2. The selenocarbamates are white solids, stable to chromatographic separations (silica-gel), with the exception of the 2,6-dimethylphenyl selenocarbamate of cedrol. This was found to be unstable upon isolation. It slowly decomposed to the corresponding olefin, which made the proper characterization very difficult. Interestingly, almost all the

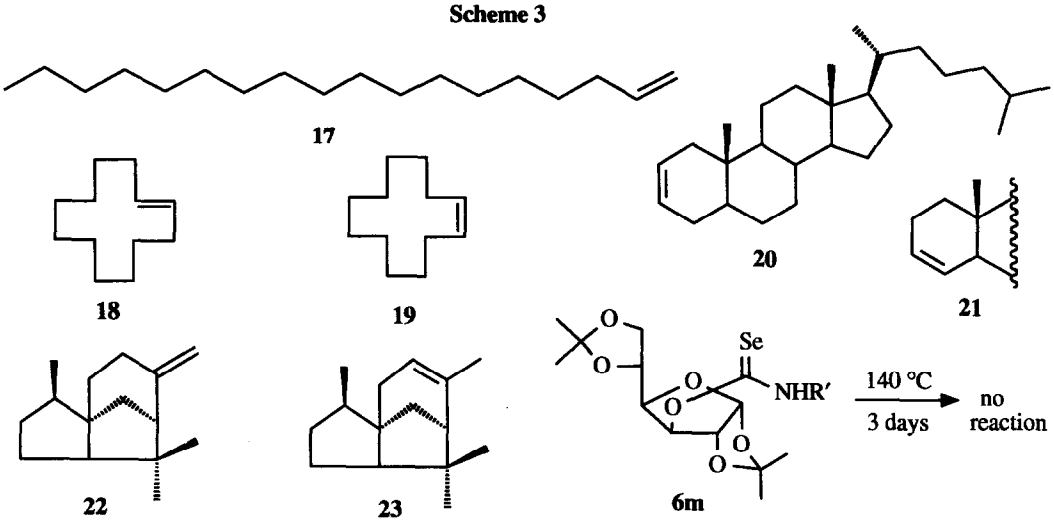
selenocarbamates showed the presence of two rotational isomers. As demonstrated in Scheme 3b, the tautomeric nature of N-C=Se ⇌ N=C-Se would induce a barrier to rotation around C-N bond. This was evidenced by the ^{1}H and ^{13}C NMR spectroscopy.

Elimination Reactions

As the formation of the corresponding olefin was the only side reaction observed during the preparation of these selenocarbamates, we decided to systematically study the Chugaev pyrolysis (olefination) of various *O*-alkylselenocarbamates. The results are summarized in Table 3. We found that upon heating the *O*-alkylselenocarbamate in $CDCl_3$ solution in a sealed NMR tube the corresponding olefin formed. In the case of the cyclododecyl selenocarbamate, only the *trans* olefin formed upon thermolysis. During this elimination reaction, selenium black precipitated out. The GC-MS analysis of the reaction mixtures indicated the presence of the corresponding amine ($R'NH_2$) in about 80-100 % yield, the other by product being the isocyanate (R'N=C=O), observed in 0-20 % yield.



Scheme 3



The rates of olefin formation (elimination) of cyclododecyl selenocarbamates **6 b-g** seemed to be somewhat substituent (*N*-substitution) dependent. The rates followed the (decreasing) order: *p*-Cl-C_6H_4 > *p*-F-C_6H_4 > Ph > *p*-MeO-C_6H_4 > 2,6-$(Me)_2$-C_6H_3 > *c*-C_6H_{11}. the higher the temperature of the reaction, the faster was the elimination. The effect of acid was also studied, as the olefin formation took

Table 3

% olefin formation[a] at: / Selenocarbamate R′:	6d Cl–	6e F–	6c H–	6g MeO–	6f	6b
80 °C, 4 hours	20.7	15.6	13.3	10.3	4.0	2.0
80 °C, 8 hours	32.3	25.8	21.0	17.1	9.1	5.1
80 °C, 12 hours	69.8	52.1	47.2	39.9	17.4	8.1
80 °C, 24 hours	.....		70.0	.....		
80 °C, 48 hours	.....		100	.....		
120 °C, 2 hours	.....		100[a]	.....		

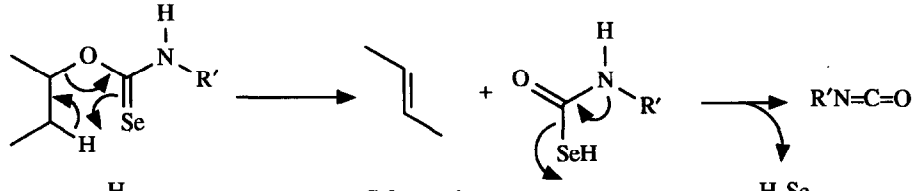
[a] Determined by ^{1}H NMR

place even at room temperature in the presence of CF_3CO_2H, as documented in Table 4. Quantitative olefination took place in the presence of 14 equivalents of trifluroacetic acid after about one day. Treatment of the selenocarbamate with trifluoracetic acid at higher temperature (100 °C) gave even faster eliminations. However, when the amount of acid is increased or when treated with acid at higher temperature, both the *cis* and *trans* cyclododecenes **18**, **19** formed. Similar trend was also observed in the case of cholestanyl derivative **6h**, as **20** and **21** formed in approximately equal amounts. The half lives of the elimination reactions of **6i**, **6j**, and **6k** were found to be 4.5 hrs, 4.5 hrs, and 7 hrs respectively, when treated with 1 eq. of CF_3CO_2H at 100 °C. The ratios of olefins **20** : **21** in these experiments were found to be 2, 2 and 3 respectively. This is likely to be due to the formation of carbocationic intermediate. The nature of substitution on the oxygen also had an effect on the rate of elimination. The selenocarbamate of tertiary alcohol eliminated much faster than the secondary, which in turn was faster than the primary. The conformational constraints also had a profound effect on the elimination reaction, as the selenocarbamate of the diacetone glucose did not eliminate even after 3 days at 140 °C and only the starting material was recovered.

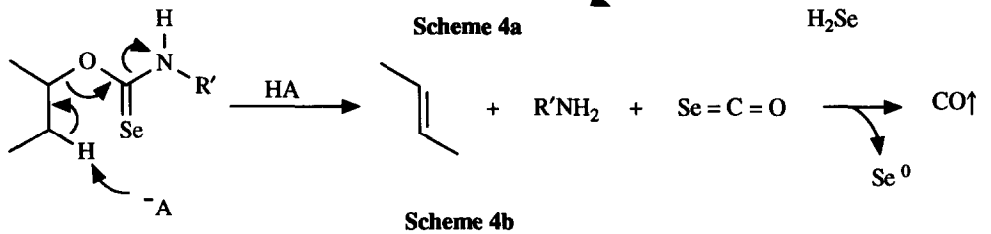
From these observations, it seemed that the mechanism of the elimination was not a simple one. Two competing pathways, depicted in Schemes 4a and b, can be postulated to explain the results of the elimination. The presence of an electron withdrawing group increased the tendency to elimination. This in turn provided more amine formation as per the mechanism proposed in Scheme 4b. The olefination reaction was attempted in the presence of a strong base like *t*-butyltetramethyl guanidine, which did not induce any elimination. However, when treated with excess methyl iodide in the presence of

Table 4 Acid mediated olefination of the selenocarbamate **6b**

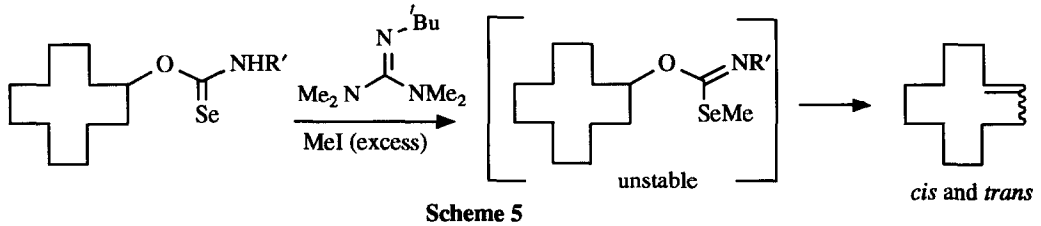
Entry	no. of equivalents of CF_3CO_2H added	Reaction Time	% starting material unreactted	% Olefin formation
1	2	10 hours	95	5
2	2	24 hours	95	5
3	4	10 hours	70	30
4	14	10 hours	11	89
5	14	24 hours	-	100



Scheme 4a



Scheme 4b



Scheme 5

t-butyltetramethyl guanidine, mixture of *cis* and *trans* olefins formed. Initial formation of selenomethyl derivative was observed by NMR, which subsequently eliminated. Any attempt to isolate the adduct failed as it resulted in the olefin formation.

Radical Deoxygenation

Recently, Nishimiya and colleagues have reported the deoxygenation of alcohols using isothiocyanates. There are some limitations of their procedure. The thionocarbamates of primary and

secondary alcohols were heated up to 140 °C in a sealed tube. Also, no tertiary alcohols were attempted. As we had at our hand a better understanding of the stability of various selenocarbamates, we turned our attention to their radical chemistry. In view of our continued interest in the development of a better method for radical deoxygenation of tertiary alcohols[16], we decided to examine the deoxygenation of the selenocarbamate of cedrol. The main limitations of the Barton-McCombie deoxygenation of tertiary alcohols are that the corresponding xanthates are difficult to isolate and purify, as they tend to eliminate quite readily. This is especially a problem, when the desired derivatives are liquids. Whereas, the selenocarbamates were found to be easily crystallizable solids. Amongst all the derivatives at hand, we found the cyclohexyl selenocarbamate of cedrol stable enough for our needs.

We carried out the radical deoxygenation as shown in Scheme 6. The results are summarized in Table 5. The deoxygenation reactions of selenocarbamates in general, were found to be far more

Table 5

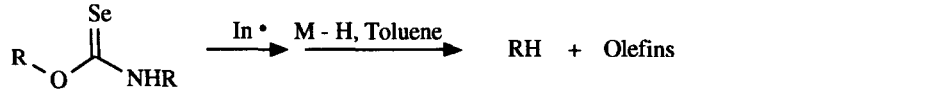
Entry	Selenocarbamate	Intiation Conditions	H-atom donor	no. of Equivalents	Products RH (Yields %)	Products Olefins (Yields %)
1	**6o**	Et_3B / O_2 , r.t. 1.2 eq.	Bu_3SnH	2	**25** (50)	**22+23** (50)
2	**6o**	Et_3B / O_2 , r.t. 2.4 eq.	Bu_3SnH	3	**25** (65)	**22+23** (35)
3	**6o**	Et_3B / O_2 , r.t. 3.6 eq.	Bu_3SnH	4	**25** (70)	**22+23** (30)
4	**6o**	Et_3B / O_2 , r.t. 1.5 eq.	Ph_2SiH_2	3	**25** (25)	**22+23** (75)
5	**6o**	AIBN, 110 °C 0.2 eq.	Bu_3SnH	2.5	**25** (33)	**22+23** (67)
6	**6b**	Et_3B / O_2 , r.t. 2.0 eq.	$(EtO)_2\overset{O}{\overset{\|\|}{P}}H$	2.5	**27** (0)	**18+19** (100)
7	**6b**	Et_3B / O_2 , r.t. 1.5 eq.	Bu_3SnH	2.5	**27** (67)	**18+19** (33)
8	**6b**	Et_3B / O_2, 0 °	Bu_3SnH	2.5	**27** (0)	**18+19** (100)
9	**6b**	AIBN, 110 °C	Bu_3SnH	2.5	**27** (25)	**18+19** (75)

sluggish than xanthates. They required larger concentrations of both the initiators and H-atom donor agents. We found that triethylborane/oxygen[17] along with tinhydride was the best system for the deoxygenation of the selenocarbamate of cedrol. Nevertheless, they are more reactive towards free radical reactions, compared to their sulfur counterparts.

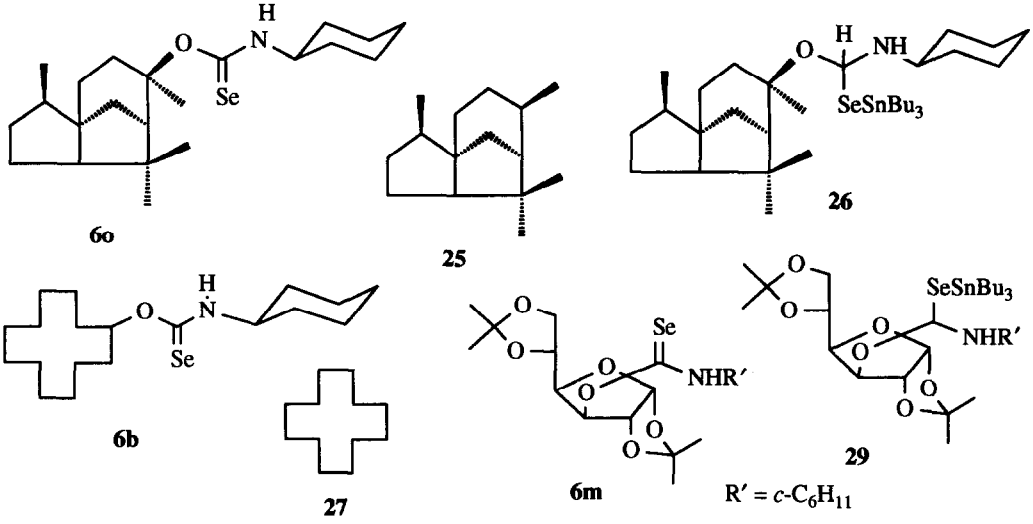
Interestingly, we also observed the addition product of tributyltin radical to the C=Se bond in **6o**, which did not undergo homolytic cleavage of the C-O bond. Instead, it abstracted a H-atom and gave the adduct **26**. This was not isolable as it eliminated upon any attempts at isolation. However, upon aqueous

work-up of the addition products of **6b** and **6o**, we were able to isolate and characterize the corresponding formates. More striking example of this unusual characteristic was found when the selenocarbamate **6m** was subjected to the deoxygenation conditions. We found that two ^{13}C signals (of two rotational isomers) at 189 and 191 ppm due to the C=Se, disappeared upon treatment with the tin radical. A new signal at 140 ppm appeared, which was attributed to the tetrahedral carbon centered intermediate **29**. The results of these preliminary investigations suggested that the selenocarbamates, unlike the thionocarbamates are reactive towards the radical deoxygenations, however, the limitation being that the adduct radical is exceptionally stable radical and hence homolytic cleavage of the carbon-oxygen bond does not take place. With the thought that this would require higher temperatures, we carried out these reactions at higher temperatures, as reported in Table 5. We found larger amounts of olefin formation.

In conclusion, it would be important to point out that the here-in reported studies on the syntheses of isoselenocyanate and selenocarbamate and their reactivities are by no means optimized and complete. It is conceivable that with the choice of proper *N*-substitution a thermally more stable *O*-alkylselenocarbamate would offer the necessary reactivity for complete deoxygenation. This would be particularly useful for the radical chemistry of tertiary alcohols.



Scheme 6



Experimental Section

General methods. Melting points were determined with a Kofler hot-stage melting point

apparatus and are uncorrected. Proton (chemical shifts referenced to TMS at δ 0.00) and ^{13}C (referenced to $CDCl_3$ at δ 77.00) NMR experiments were carried out at room temperature on a Varian XL-200 or a Gemini-200 spectrometer operating at 200 and 50 MHz, respectively, using 5 mm tubes. Infrared spectra were recorded on a Perkin-Elmer 881 spectrophotometer. GC-MS analyses were performed on a Hewlett-Packard 5790A series gas chromatograph equipped with a quadruple mass-selective detector. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA. Solvents were used either as purchased or dried and purified by standard methods. The optical rotations were measured on the JASCO digital polarimeter Model DIP-360. The concentrations reported as *c* for the specific rotations are in gr/mL %.

General Procedure for the Preparation of Isoselenocyanate 7.

In a 3-neck flask equipped with a magnetic stirrer and an addition funnel, 50 mL of toluene 10 mmol of the formamide was placed. This solution was cooled in an ice bath and stirred under argon. Triethyl amine (40 mmol) was added and 15 mmol of selenium black (powder) was added to the stirred solution. The addition funnel was charged with 15 mmol of phosgene as solution in toluene. The phosgene solution was added slowly to the stirred suspension (kept in an ice-bath) over a period 30 minutes. An exothermic reaction took place. After the addition was over, the suspension was brought to reflux. The progress of the reaction was followed by tlc. Typically, one day was required for the completion of the reaction. The reaction mixture was filtered and washed with several portions of toluene. The filtrate was concentrated and fractionated over silica gel using hexanes as eluent to afford the isoselenocyanate. All the isoselenocyanates were characterized by ^1H and ^{13}C NMR and IR spectroscopy. The new compounds were also tested for the elemental analysis.

***N*-cyclohexylisoselenocyanate 7a.**

This isoselenocyanate was isolated in 78 % yield as an oil. Literature reported the m.p. 4-5 ^0C. Their spectroscopic data were unavailable in the literature.[7a,10] ^1H NMR ($CDCl_3$) δ: 3.8 (m, 1H), 2.0-1.6 (m, 6H), 1.5-1.3 (m, 4H). ^{13}C NMR ($CDCl_3$) δ: 55.7, 32.5, 24.7, 22.9. IR ($CHCl_3$) υ: 2156 (NCSe).

***N*-phenylisoselenocyanate 7b.**

This isoselenocyanate was isolated in 79 % yield as an oil. Literature reported the m.p. 14-16 ^0C. The spectroscopic data were unavailable in the literature.[10] ^1H NMR ($CDCl_3$) δ: 7.25-7.4 (m, 5H). ^{13}C NMR ($CDCl_3$) δ: 129.4, 128.0, 126.0.

***N*-4-chlorophenylisoselenocyanate 7c.**

This isoselenocyanate was isolated in 65 % yield as crystalline solid, m.p. 69-70 ^0C. The literature reported the m.p. 68-70 ^0C. The spectroscopic data were unavailable in thhe literature. ^1H NMR ($CDCl_3$) δ: 7.35 (d, J=8 Hz, 2H), 7.22 (d, J=8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 133.7, 129.7, 127.2.

***N*-(4-fluorophenyl)isoselenocyanate 7d.**

This isoselenocyanate was isolated in 44 % yield as crystalline solid, m.p. 44-46 ^0C. ^1H NMR

($CDCl_3$) δ: 7.3 (m, 2H), 7.15 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 161.4 (d, J_{C-F}=249.1 Hz), 127.8 (d, J_{C-F}=8.5 Hz), 116.7 (d, J_{C-F}=23.5 Hz). IR (film) υ: 2125, 1492, 1229, 1206, 1146, 1088, 833, 693. Anal. Calcd. for C_7H_4FNSe: C, 42.02; H, 2.02. Found: C, 42.13, H, 2.04.

***N*-(2,6-dimethylphenyl)isoselenocyanate 7e.**

This isoselenocyanate was isolated in 68 % yield as crystalline solid, m.p. 34-36 °C. ^1H NMR ($CDCl_3$) δ: 7.05 (m, 3H), 2.38 (s, 6H). ^{13}C NMR ($CDCl_3$) δ: 135.41, 127.88, 127.58, 18.59. Anal. Calcd. for C_9H_9NOSe: C, 51.44; H, 4.32; N, 6.67. Found: C, 51.29, H, 4.29; N, 6.66.

***N*-(4-methoxyphenylisoselenocyanate 7f.**

This isoselenocyanate was isolate in 50 % yield as crystalline solid m.p. 42-43 °C. The literature reported the m.p. 44-45 °C. The spectroscopic data were unavailable in the literature. ^1H NMR ($CDCl_3$) δ: 7.25 (d, 2H, J=10 Hz), 6.85 (d, 2H, J=10 Hz), 3.81 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 159.0, 127.3, 114.7, 55.5.135.41, 127.88, 127.58, 18.59. IR (film) υ: 3026, 2919, 2735, 2270, 2097, 1588, 1458, 1376, 1259, 1189, 1163, 1131, 1068, 1029.

General Procedure for the Preparation of *O*-Alkylselenocarbamate 6.

Appropriate alcohol (1 equivalent) was added to a mixture of potassium hydride (3 equivalent) in anhydrous THF. The mixture was allowed to react in an inert atmosphere for about 2 hours. The solution was deccanted from the solid residue and transfered slowly to a THF solution of the appropriate isoselenocyanate (1.2 eq.) and stirred at room temperature for 4 hours. The reaction was followed by tlc for the disappearance of the starting material. At the end of reaction, the solution was diluted with ether, and extracted with water, brine and concentrated to afford an oil. Recrystallization with hexanes and dichloromethane gave a white crystalline solid. The selenocarbamates of cyclododecanol and the octadecanol were stable enough for, and hence purified by, chromatographic separations over silica gel.

The *N*-cyclohexylselenocarbamate of octadecanol 6a.

This was isolated in 60 % yield, recrystallized from CH_2Cl_2 and hexanes, m.p. 60-61 °C. ^1H NMR ($CDCl_3$) δ: 7.15 (m, 1H), 6.55 (m, 1H), 4.58 (t, J=6.7 Hz, 2H) 4.5 (t, J=6.7 Hz, 2H), 4.22 (m, 1H), 3.63 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 192.32, 190.01, 75.74, 73.51, 55.36, 53.12, 32.17, 32.09, 32.02, 31.84, 29.62, 29.45, 29.28, 29.23, 29.11, 28.59, 28.53, 25.76, 25.29, 25.10, 24.61, 24.49, 22.61, 14.05. IR (CH_2Cl_2) υ: 3944, 3690, 3365, 3054, 2987, 2928, 2855, 2684, 2520, 2411, 2303, 2125, 2055, 1602, 1504, 1419, 1258, 1170. Anal calcd. for $C_{25}H_{49}NOSe$: C, 65.47, H, 10.77, N, 3.05; Found: C, 65.55, H, 10.81, N, 2.98.

***O*-Cyclododecyl-*N*-cyclohexylselenocarbamate 6b.**

This was isolated in 74% yield. It was recrystallized from CH_2Cl_2 and hexanes, m.p. 120-121 °C. The compound exhibits two rotational isomers. ^1H NMR ($CDCl_3$) [both rotamers] δ: 1.1-2.1 (m, 32H), 3.7-3.6 and 4.2-4.3 (1H, m), 5.6-5.8 (1H, m), 6.5 and 7.3 (1H, m, NH). ^{13}C NMR ($CDCl_3$) [both rotamers] δ: 192.1 and 189.5 (C=Se), 85.09 and 81.7 (C-O), 55.08, 52.8 (C-N), 32.02, 31.95, 28.6, 28.8,

25.0, 25.1, 24.3, 24.4, 24.1, 23.8, 23.9, 23.5, 23.0, 23.2, 22.8, 20.5, 20.7. IR ($CHCl_3$) υ: 3405, 3367, 2935, 1501, 1172. Anal. Calcd. for $C_{19}H_{35}NOSe$: C, 61.27; H, 9.47; N, 3.76. Found: C, 61.38; H, 9.54; N, 3.76.

***O*-Cyclododecyl-*N*-phenylselenocarbamate 6c.**

The compound was obtained in 82% yield upon isolation. It was recrystallized using CH_2Cl_2 and hexanes, m.p. 138-139 ^{0}C. ^{1}H NMR ($CDCl_3$) δ: 9.35 (s, 1H, NH), 7.4-7.15 (m, 5H), 5.8 (m, 1H), 2.0-1.7(m, 4H), 1.6-1.3 (m, 18H). ^{13}C NMR ($CDCl_3$) δ: 190.4, 137.2, 129.2, 125.6, 121.6, 86.9, 28.6, 24.0, 23.7, 23.1, 22.9, 20.6. IR (film) υ: 3388, 2935, 1508, 1400, 1323, 1210, 1165, 1142. MS calcd for $C_{19}H_{29}NOSe$, 366; found, (no M^+), 166, 109, 96, 82, 67. Anal. Calcd. for $C_{19}H_{29}NOSe$: C, 62.28; H, 7.97; N, 3.82. Found: C, 62.15; H, 8.04; N, 3.79.

***O*-Cyclododecyl-*N*-(4-chlorophenyl)selenocarbamate 6d.**

The compound was obtained in 88% yield upon isolation. It was recrystallized using CH_2Cl_2 and hexanes, m.p. 143-144 ^{0}C. ^{1}H NMR ($CDCl_3$) δ: 9.57 (bs, 1H), 7.35-7.2 (m, 4H), 5.76 (m, 1H), 1.9-1.3 (m, 22H). ^{13}C NMR ($CDCl_3$) δ: 189.9, 135.5, 130.8, 129.1, 128.9, 87.0, 28.7, 24.1, 23.8, 23.2, 23.0, 22.7. IR (film) υ: 3386, 2937, 1587, 1497, 1389, 1350, 1209, 1164, 1142. MS calcd for $C_{19}H_{28}ClNOSe$, 400; found, 400 (M^+), 166, 96, 82, 67. Anal. Calcd. for $C_{19}H_{28}ClNOSe$: C, 56.93; H, 7.04; N, 3.49. Found: C, 56.73; H, 7.08; N, 3.43.

***O*-Cyclododecyl-*N*-(4-fluorophenyl)selenocarbamate 6e.**

This selenocarbamate was obtained in 91% yield upon isolation. It was recrystallized using CH_2Cl_2 and hexanes, m.p. 142-143 ^{0}C. ^{1}H NMR ($CDCl_3$) δ: 9.5 (bs, 1H), 7.2-7.3 (m, 2H), 6.9-7.1 (m, 2H),5.75 (m, 1H), 1.9-1.7 (m, 4H), 1.6-1.2 (m, 18H). ^{13}C NMR ($CDCl_3$) δ: 189.7, 133.0, 123.0 (d, 8Hz), 116.0 (d, 21.1Hz), 86.7, 28.7, 24.1, 23.8, 23.2, 23.0 20.7. IR (film) υ: 3383, 2924, 1498, 1393, 1226, 1200, 1139, 829. MS, calcd. for $C_{19}H_{28}FNOSe$, 384; found, (no M^+), 166, 109, 96, 82, 67, 55. Anal. Calcd. for $C_{19}H_{28}FNOSe$: C, 59.36; H, 7.34; N, 3.64. Found: C, 59.49; H, 7.38; N, 3.58.

***O*-Cyclododecyl-*N*-(2,6-dimethylphenyl)selenocarbamate 6f.**

This was isolated in 69% yield. It was recrystallized from CH_2Cl_2 and hexanes, m.p. 147-148 ^{0}C. The compound exhibits two rotational isomers, ratio 4:1. ^{1}H NMR ($CDCl_3$) [both rotamers] δ: 8.7 and 7.8 (bs, 1H), 7.2-7.0 (m, 3H), 5.8-5.6 (m, 1H), 2.26 and 2.23 (s, 6H), 1.8-1.1 (m, 22H). ^{13}C NMR ($CDCl_3$) [both rotamers] δ: 194.8, 191.7, 135.5, 134.9, 128.5, 128.2, 128.0, 85.4, 83.0, 28.8, 28.9, 23.9, 23.8, 23.6, 23.5, 23.0, 22.9, 20.5, 20.8, 18.1. IR (film) υ: 3386, 2935, 1483, 1512, 1196, 1041. MS calcd for $C_{21}H_{33}NOSe$: 394; found, (no M^+), 317, 166, 96, 67. Anal. Calcd. for $C_{21}H_{33}NOSe$: C, 63.94; H, 8.43; N, 3.55. Found: C, 64.00; H, 8.49; N, 3.98.

***O*-Cyclododecyl-*N*-(4-methoxyphenyl)selenocarbamate 6g.**

This was obtained in 89% yield upon isolation. It was recrystallized using CH_2Cl_2 and hexanes, m.p. 137-139 ^{0}C. ^{1}H NMR ($CDCl_3$) δ: 9.2 (bs, 1H, NH), 7.2 (d, J=8.8 Hz, 2H), 6.85 (d, J=8.8 Hz, 2H),

5.7 (m, 1H), 1.3-1.9 (m, 22H). ^{13}C NMR ($CDCl_3$) δ: 189.3, 157.2, 130.2, 123.4, 114.0, 86.4, 55.3, 28.7, 24.2, 23.9, 23.2, 23.0, 20.7. IR (film) υ: 3391, 2937, 1509, 1400, 1352, 1240, 1209, 1162, 1143. MS calcd for $C_{20}H_{31}NO_2Se$, 396; found, 396 (M^+), 327, 281, 166, 96, 67. Anal. Calcd. for $C_{20}H_{31}NO_2Se$: C, 60.59; H, 7.88; N, 3.53. Found: C, 60.47, H, 7.92; N, 3.49.

_N_-cyclohexylselenocarbamate of cholestanol 6h.

This selenocarbamate was isolated in 80% yield. It was recrystallized using CH_2Cl_2 and hexanes, m.p. 210-212 ^{0}C. The compound exhibits two rotational isomers. The specific rotation was found to be, $[\alpha]_D^{20}$ = +6.05 (*c* 5.14, $CHCl_3$). ^1H NMR [both rotamers] ($CDCl_3$) δ: 7.18 (d, J=8 Hz, 1H), 6.46 (d, J=8 Hz, 1H), 5.65 (m, 1H), 4.45 (m, 1H), 3.65 (m, 1H), 0.89 (s,3H). ^{13}C NMR [both rotamers] ($CDCl_3$) δ: 191.12, 188.81, 85.54, 82.48, 56.31, 56.16, 55.19, 54.08, 52.87, 44.35, 42.52, 39.90, 39.46, 36.52, 36.10, 35.74, 35.42, 35.30, 33.84, 32.15, 31.89, 28.55, 28.19, 27.96, 27.36, 25.33, 25.18, 24.64, 24.48, 24.15, 23.76, 22.78, 22.52, 21.19, 18.62, 12.27, 12.16, 12.03. IR (film) υ: 3407, 3372, 2937, 2860, 1614, 1501, 1447, 1411, 1382, 1363, 1347, 1168, 1141, 1068, 1004. Anal. Calcd. for $C_{34}H_{59}NOSe$: C, 70.80; H, 10.31; N, 2.43. Found: C, 70.96, H, 10.27; N, 2.39.

The _N_-phenylselenocarbamate of cholestanol 6i.

This selenocarbamate was isolated in 65 % yield. It was recrystallized using CH_2Cl_2 and hexanes, m.p. 175-178 ^{0}C. The compound exhibits two rotational isomers. The specific rotation was found to be, $[\alpha]_D^{20}$ = +1.33 (*c* 4.57, $CHCl_3$). ^1H NMR [both rotamers] ($CDCl_3$) δ: 9.4 (m, 1H), 7.15-7.10 (m, 5H), 5.45 (m, 1H), 0.85-2.20 (m, 47H). ^{13}C NMR [both rotamers] ($CDCl_3$) δ: 189.38, 137.02, 129.05, 125.54, 121.47, 86.98, 56.28, 56.12, 54.04, 44.38, 42.49, 39.86, 39.43, 36.49, 36.07, 35.71, 35.37, 35.29, 33.65, 31.85, 28.49, 28.16, 27.94, 27.23, 24.13, 23.74, 22.77, 22.51, 21.17, 18.60, 12.24, 12.01. IR (film) υ: 3375, 2935, 2856, 1584, 1498, 1434, 1393, 1340, 1205, 1143, 1124, 1001. Anal. Calcd. for $C_{34}H_{53}NOSe$: C, 71.55; H, 9.36; N, 2.45. Found: C, 71.56, H, 9.31; N, 2.44.

_N_-(4-chlorophenyl)selenocarbamate of cholestanol 6j.

This selenocarbamate was isolated in 87 % yield. It was recrystallized using CH_2Cl_2 and hexanes, m.p. 207-209 ^{0}C. The compound exhibits two rotational isomers. The specific rotation was found to be, $[\alpha]_D^{20}$ = +1.24 (*c* 3.6, $CHCl_3$). ^1H NMR [both rotamers] ($CDCl_3$) δ: 9.05 (bs, 1H), 7.30 (m, 4H), 5.45 (m, 1H), 0.60-2.22 (m, 47H). ^{13}C NMR ($CDCl_3$) δ: 189.50, 129.24, 129.17, 129.13, 122.76, 56.36, 56.21, 54.12, 44.48, 42.58, 39.95, 39.52, 36.56, 36.15, 35.79, 35.46, 35.39, 33.72, 31.93, 28.58, 28.25, 28.03, 27.30, 24.21, 23.82, 22.85, 22.58, 22.25, 18.68, 12.33, 12.09. IR (film) υ: 3019, 2971, 2400, 1516, 1422, 1209, 1044. The elemental analysis of this compound gave unsatisfactory results.

_N_-(4-flurophenyl)selenocarbamate of cholestanol 6k.

This selenocarbamate was isolated in 70 % yield. It was recrystallized using CH_2Cl_2 and hexanes, m.p. 183-185 ^{0}C. The compound exhibits two rotational isomers. The specific rotation was found to be, $[\alpha]_D^{20}$ = +1.14 (*c* 3.56, $CHCl_3$). ^1H NMR [both rotamers] ($CDCl_3$) δ: 9.00 (s, 1H), 7.25 (m,

2H), 7.05 (m, 2H), 5.45 (m, 1H), 0.85-2.2 (m, 47H). ^{13}C NMR ($CDCl_3$) δ: 189.5, 123.69, 123.52, 116.2, 115.74, 87.23, 56.34, 54.10, 44.45, 42.56, 39.92, 39.49, 36.13, 35.77, 35.44, 35,36, 33.69, 31.90, 28.56, 28.21, 27.99, 27.26, 24.18, 23.79, 22.81, 22.55, 21.22, 18.65, 12.28, 12.06. IR (film) υ: 3385, 3052, 2985, 2867, 2305, 1507, 1420, 1257, 1204, 1152, 1006. Anal. Calcd. for $C_{34}H_{52}NOSe$: C, 69.37; H, 8.90; N, 2.38. Found: C, 69.23, H, 8.88; N, 2.34.

***N*-(2,6-dimethylphenyl)selenocarbamate of cholestanol 6l.**

This selenocarbamate was isolated in 67 % yield. It was recrystallized using CH_2Cl_2 and hexanes, m.p. 230-232 ^0C. The compound exhibits two rotational isomers. The specific rotation was found to be, $[\alpha]_D^{20}$ = +18.65 (*c* 1.7, $CHCl_3$). ^1H NMR [both rotamers] ($CDCl_3$) δ: 8.45 (m, 1H), 7.80 (m, 1H), 7.08 (m, 3H), 5.35 (m, 1H), 2.26 (s, 3H), 2.23 (s, 3H), 0.87 (s, 3H), 0.84 (s, 3H), 0.72 (d, J=7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 190.90, 135.26, 134.58, 128.32, 128.09, 86.18, 56.30, 56.16, 54.04, 44.36, 42.51, 39.88, 38.47, 36.47, 36.11, 35.74, 35.39, 35.27, 33.57, 31.88, 28.50, 28.19, 27.47, 27.16, 24.15, 23.77, 22.79, 22.53, 21.17, 18.62, 18.33, 12.21, 12.02. IR (film) υ: 3391, 3019, 2948, 2867, 2401, 1614, 1483, 1347, 1212, 901, 767. Anal. Calcd. for $C_{36}H_{57}NOSe$: C, 72.21; H, 9.59; N, 2.34. Found: C, 72.46, H, 9.66; N, 2.33.

***N*-cyclohexylselenocarbamate of diacetone glucose 6m**

This selenocarbamate was isolated in 81 % yield. It was recrystallized using CH_2Cl_2 and hexanes, m.p. 146-148 ^0C. The compound exhibits two rotational isomers. The specific rotation was found to be, $[\alpha]_D^{20}$ = -4.50 (*c* 1.49, $CHCl_3$). ^1H NMR [both rotamers] ($CDCl_3$) δ: 7.8 and 6.8 (d, J=4.5, 1H), 5.91 and 5.86 (d, J=2.68, 1H), 4.90 and 4.77 (d, J=3.7, 1H), 4.02-4.29 (m, 4H), 1.2-1.6 (s, 12H). ^{13}C NMR ($CDCl_3$) δ: 190.84, 189.02, 112.37, 112.25, 109.50, 109.29, 104.63, 86.12, 83.76, 83.67, 83.59, 79.93, 79.31, 72.39, 72.32, 67.55, 66.78, 55.95, 53.73, 32.30, 32.00, 31.89, 31.79, 26.74, 26.64, 26.58, 26.17, 25.28, 25.21, 24.96, 24.54, 24.51. IR (film) υ: 3359, 2984, 2939, 1508, 1395, 1373, 1211, 1162, 1135, 1075, 1019. Anal. Calcd. for $C_{19}H_{31}NO_6Se$: C, 50.89; H, 6.97; N, 3.12. Found: C, 50.98, H, 6.98; N, 3.08.

***N*-phenylselenocarbamate of diacetone glucose 6n.**

This selenocarbamate was isolated in 77 % yield. It was recrystallized using CH_2Cl_2 and hexanes, m.p. 80-82 ^0C. The specific rotation was found to be, $[\alpha]_D^{20}$ = -5.60 (*c* 1.39, $CHCl_3$). ^1H NMR [both rotamers] ($CDCl_3$) δ: 9.50 (bs, NH, 1H), 7.20-7.40 (m, 5H), 5.86 (m, 2H), 4.90 (d, J=3.8, 1H), 3.85-4.35 (m, 4H), 1.55 (s, 3H), 1.41 (s, 3H), 1.34 (s, 3H), 1.26 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 129.4, 126.9, 122.9, 112.6, 109.5, 104.8, 83.6, 79.8, 72.3, 67.3, 26.6, 26.5, 26.1, 24.9. IR (film) υ: 3393, 3020, 2401, 1594, 1508, 1421, 1383, 1333, 1216, 1077. Anal. Calcd. for $C_{19}H_{25}NO_6Se$: C, 51.59; H, 5.70; N, 3.17. Found: C, 51.66, H, 5.75; N, 3.15.

***N*-cyclohexylselenocarbamate of cedrol 6o.**

This selenocarbamate was isolated in 78 % yield. It was recrystallized using CH_2Cl_2 and

hexanes, m.p. 122-123 ^{0}C. The compound exhibits two rotational isomers. ^{1}H NMR [both rotamers] (C_6D_6) δ: 7.75 (m, 1H), 6.10 (m, 1H), 4.50 (m, 1H), 4.02 (d, J=5.1, 1H), 3.83 (d, J=4.8, 1H), 3.55 (m, 1H), 2.00 (s, 3H), 1.93 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H), 1.09 (s, 3H), 0.78 (d, J=6.9, 3H), 0.77 (d, J=7.04, 3H). ^{13}C NMR (C_6D_6) δ: 188.02, 185.74, 93.87, 92.65, 57.36, 57.22, 56.11, 55.37, 54.29, 54.02, 53.38, 43.64, 43.54, 41.37, 41.31, 37.25, 35.69, 35.42, 35.35, 32.15, 32.11, 31.56, 31.44, 28.19, 28.14, 27.36, 27.25, 26.80, 26.73, 25.66, 25.50, 25.42, 25.04, 15.75. IR (film) υ: 3400, 3369, 2937, 1492, 1449, 1391, 1375, 1358, 1347, 1309, 1246, 1198, 1174, 1142, 1091, 1081, 1042, 1004, 982, 889, 706. Anal. Calcd. for $C_{22}H_{37}NOSe$: C, 64.37; H, 9.08; N, 3.41. Found: C, 64.36, H, 9.11; N, 3.47.

General Procedure for Radical Deoxygenation

The Selenocarbamate (1 eq.) was dissolved in dry benzene or toluene. The solution was stirred under argon at the desired temperature. Tributyltin hydride (1.5 eq.) was added, and then triethyl borane (0.25 eq.) was added. Dry air was injected to initiate the reaction. The progess of the reaction was followed by tlc. If the reaction was found to contain the starting selenocarbamate, the atmosphere in the reaction flask was changed back to the inert atmosphere by bubbling argon through the solution. Addition of triethyl borane (and also tin hydride, if needed) followed by O_2-initiation was continued until the disappearance of the starting material. The crude reaction mixture was analyzed by GC-MS, NMR and IR. Fractionation over silica gel with hexanes as eluent, provided pure fractions containing deoxygenated and the olefins. All the deoxygenated hydrocarbons and the olefins are known compounds, and the characterization was done by comparison with the literature data.

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