Ring-closure Reactions of Alkenyl Oximes Induced by Persulfate Anion Oxidation of Diphenyl Diselenide. Formation of 1,2-Oxazines and Cyclic Nitrones

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A strongly electrophilic phenylselenenylating agent is produced from the reaction of diphenyl diselenide with ammonium persulfate, in the presence of trifluoromethanesulfonic acid, in acetonitrile or nitromethane, at room temperature. This reagent induces regioselective ring-closure reactions on γ-alkenyl oximes to afford (phenylseleno)methyl-substituted 1,2-oxazines and/or cyclic nitrones, indicating that, depending on its geometry, the oxime group can act either as an oxygen or as a nitrogen nucleophile. However, the ratio of the two heterocyclic reaction products does not reflect the *Z*/*E* ratio of the starting oximes, the formation of the five-membered cyclic nitrone being largely preferred over the six-membered 1,2-oxazine. Several derivatives which confirm the proposed structures and at the same time exemplify the synthetic utility of the products obtained with this reaction have also been prepared.

We have recently introduced the use of phenylselenenyl sulfate [$(PhSe)_2SO_4$] as a strong electrophilic selenenylating agent which can be easily produced from the reaction of PhSeSePh with ammonium persulfate.[1] This reagent has found wide synthetic application[2,3] and it has also been employed to effect several ring-closure reactions.[4,5] Selenoetherification of allyl derivatives of alcohols, 1,3-dicarbonyl compounds, amides, thioamides, and ketones as well as selenolactonization of allyl derivatives of acids, amides and nitriles can all be easily carried out with excellent results.[4] An even more efficient selenenylating agent can be obtained by adding trifluoromethanesulfonic acid to the mixture of PhSeSePh and ammonium persulfate, in acetonitrile or nitromethane, at room temperature. The resulting solution rapidly turns from deep red to colourless upon the addition of the above mentioned unsaturated compounds.[6]

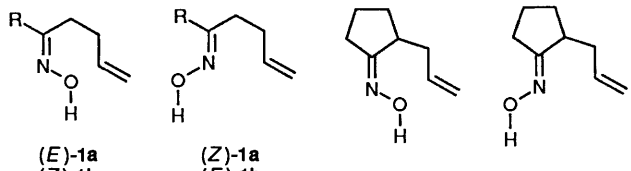
We now report that this reagent can also induce efficient ring closure of γ-alkenyl oximes to give (phenylseleno)methyl-substituted 1,2-oxazines and/or cyclic nitrones, indicating that the oxime group, depending on its geometry, can act either as an oxygen or as a nitrogen nucleophile in the intramolecular trapping of the initially formed seleniranium intermediates.

Results and Discussion

The oximes employed for the present investigation, **1a–c** and **2**, are indicated in Table 1. These were easily prepared either from the corresponding ketones (Method A) by standard methods (**1a** and **1b**), or by allylation of the corresponding methyl ketone oximes (**1a**, **1b** and **2**), according to the procedure described in the literature for the alkylation of same oximes[7] (Method B). Similarly, compound **1c** was produced by benzylation of compound **1b**.

The allylation of acetophenone oxime gave the pure *E* isomer **1a** (44% yield). In all the other cases the oximes were obtained as a mixture of *E* and *Z* isomers. In the case of oxime **1a**, prepared from the ketone in 91% yield, the pure *Z* and *E* isomers (*Z*/*E* ~ 1/9) could be obtained by column chromatography. The two isomeric oximes could also be separated in compound **2** (90% yield, *Z*/*E* ~ 2/1). On the other hand, in the cases of oximes **1b** and **1c** such a separation was not possible and the mixtures of the two isomers were directly used for the selenium-induced cyclization experiments. In the case of oxime **1b** the *Z*/*E* ratio was ~ 1/2 in the mixture derived from the ketone (89% yield) and 3/1 in the mixture obtained by allylation of acetone oxime (60% yield). Finally, oxime **1c** was obtained, in 48% yield, from the 3 : 1 mixture of the *Z* and *E* isomers of oxime **1b** and it was a 1 : 2 mixture of *Z* and *E* isomers. All these results are summarized in Table 1.

Table 1 Synthesis of the γ-alkenyl oximes **1a–c** and **2**



(*E*)-**1a** (*Z*)-**1b** (*E*)-**1c** | (*Z*)-**1a** (*E*)-**1b** (*Z*)-**1c** | (*Z*)-**2** | (*E*)-**2**

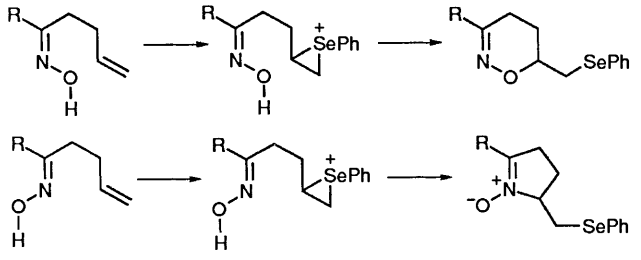
Oximes	R	Method	*Z*/*E*	Yield (%)
1a	Ph	A	1/9	91
1a	Ph	B	0/1	44
1b	Me	A	1/2	89
1b	Me	B	3/1	60
1c	$PhCH_2CH_2$	B	1/2	48
2		B	2/1	90

The selenium-induced cyclizations were carried out by adding, at room temperature, an oxime to a solution of the selenenylating agent. This was simply obtained by addition of trifluoromethanesulfonic acid to a mixture of PhSeSePh and ammonium persulfate, in acetonitrile, at room temperature. The resulting solution rapidly turns from deep red to colourless upon the addition of an oxime. The reaction of PhSeSePh with ammonium persulfate, which produces phenylselenenyl sulfate, is slow and it is usually carried out at 60–70 °C.[1–5] However, in the presence of trifluoromethanesulfonic acid the reaction is complete after a few minutes at room temperature. Under these conditions the selenenylating agent is very likely a mixture of the phenylselenenyl sulfate and phenylselenenyl trifluoromethanesulfonate. The addition of the electrophilic reagent to the carbon–carbon double bond of the γ-alkenyl oximes will produce the corresponding seleniranium intermediates, which are intramolecularly trapped by the internal nucleophile. As indicated in Scheme 1, it is expected that the configuration of the oxime will determine the nature of the reaction products. Hence,

Table 2 Synthesis of the oxazines **3** and **5** and of the nitrones **4** and **6** from the oximes **1a–c** and **2**

Oxime	*Z*/*E*	Oxazine	Yield (%)	Nitrone	Yield (%)
(*E*)-**1a**		**3a**	78		
(*Z*)-**1a**				**4a**	65
1b	1/2	**3b**	20	**4b**	58
1b	3/1	**3b**	32	**4b**	38
1c	1/2	**3c**	25	**4c**	41
2	2/1	**5**	25	**6**	51
(*Z*)-**2**		**5**	20	**6**	42
(*E*)-**2**				**6**	73

the 1,2-oxazines orginate from the isomers in which the hydroxy group lies on the same side of the chain containing the carbon–carbon double bond, and the cyclic nitrones are derived from the other isomers.

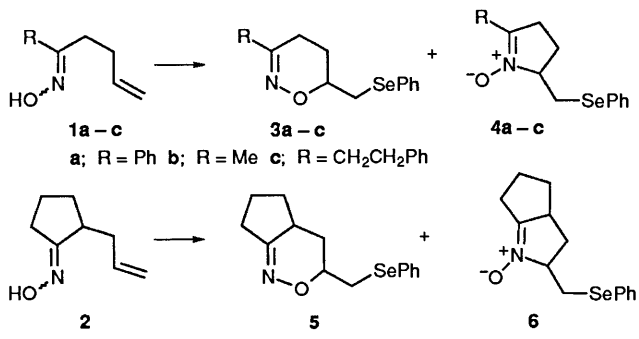


Scheme 1

Indeed the reaction of the oxime (*E*)-**1a** with the selenenylating agent afforded the 1,2-oxazine **3a** (78%) as the sole reaction product, and the isomeric (*Z*)-oxime gave exclusively the cyclic nitrone **4a** (65%). However, under the same experimental conditions, the oximes **1b** (*Z*/*E* ~ 1/2) gave products **3b** (20%) and **4b** (58%) and the oximes **1b** (*Z*/*E* ~ 3/1) afforded the two cyclization products (70% yield) in ~ 1:1 ratio. From the oximes **1c** the cyclization products **3c** and **4c** were obtained in 25 and 41% yield, respectively. Finally, from the reaction of the oximes **2** compounds **5** and **6** were formed in a 1:2 ratio, starting either from the mixture of the two isomers (76%) or from a pure *Z* isomer (62%). Compound **6** was obtained as the sole reaction product (73%) when the reaction was carried out on the pure *E* isomer **2**. All these results are summarized in Scheme 2 and in Table 2.

These results indicate that the nature of the group R influences the course of the reaction. Whereas in the case of the phenyl derivative **1a** the structure of the cyclization products depends on the geometry of the starting oximes, in the other three cases the ratios in which the 1,2-oxazines **3** and **5** and the cyclic nitrones **4** and **6** are formed do not reflect the ratios of the starting oximes. In these cases the formation of the five-membered cyclic nitrones seems to be largely preferred over that of the six-membered 1,2-oxazines. This can be explained by assuming that, under the reaction conditions employed, whereas the oximes **1a** remain configurationally stable, the other oximes suffer partial isomerization. Moreover, when the progress of the reactions was monitored by GC-MS, we observed that the ratios of the two reaction products changed slightly with time, indicating that, under the experimental conditions employed, the 1,2-oxazines partly isomerize to the cyclic nitrones.[8]

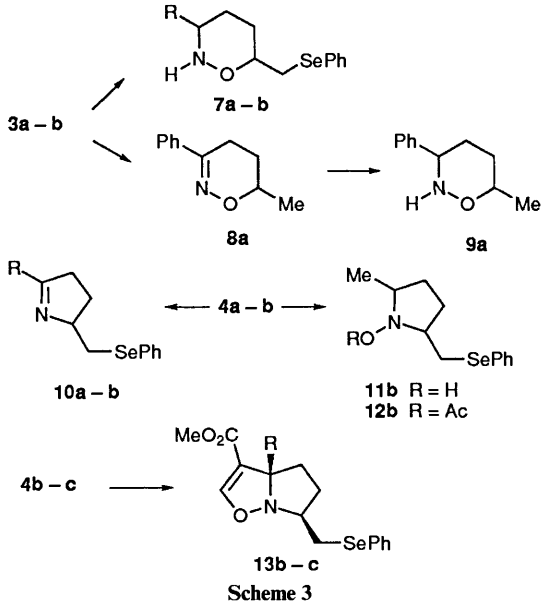
While this paper was in an advanced stage of preparation a preliminary communication by Grigg *et al.*, concerning the benzeneselenenyl halide-induced formation of cyclic nitrones from alkenyl oximes, appeared.[9] The cyclization was effected in two steps. Benzeneselenenyl bromide or chloride, in the presence of an appropriate silver salt, was used to prepare the



Scheme 2

products of addition to the double bond; these were then cyclized in the presence of anhydrous sodium hydrogen carbonate. Although the experimental conditions are quite different in the two cases, the results described in the present paper are in agreement with those reported by Grigg *et al.* An interesting conclusion reached by these authors[9] was that the oxazine:nitrone ratio is sensitive to the experimental conditions employed. The results described above bring further support to this observation.

To our knowledge these selenium-promoted cyclizations of alkenyl oximes to 1,2-oxazines and cyclic nitrones are unprecedented.[10] Moreover, they provide an easy access to two interesting reaction products which can find useful synthetic applications.

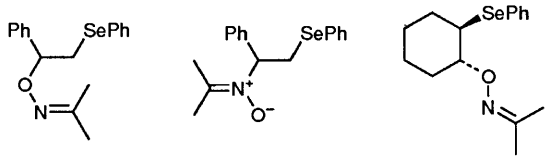


Scheme 3

As indicated in Scheme 3, the reaction of the 1,2-oxazines **3a** and **3b** with sodium cyanoborohydride afforded the reduced products **7a** (82%) and **7b** (86%), respectively. Interestingly, in both cases a single isomer was obtained. Treatment of compound **3a** with Raney nickel produced the deselenenylated 1,2-oxazine **8a** (45%) which was then reduced to compound **9a** (67%). In this case also was a single isomer formed. In contrast, the same reduction reaction of compound **4b** afforded a 2.5:1 mixture of the two isomeric cyclic hydroxylamines **11b** (90%). These could be easily separated by column chromatography and converted into the *O*-acetate **12b** in 83 and 55% yield, respectively. The deoxygenated products **10a** (60%) and **10b** (42%) were formed when the cyclic nitrones **4a** and **4b** were treated with phosphorus trichloride in chloroform. Compounds **10a** and **10b** were also observed when compounds **4a** and **4b**

were analysed by GC-MS. Similar behaviour was shown by the bicycle **6**. Finally the cyclic nitrones **4b** and **4c** were employed to effect 1,3-dipolar cycloadditions with methyl propiolate according to the procedure reported in the literature for cyclic nitrones having similar structures.[11] In both cases the reaction proceeded smoothly at room temperature to give the 2-oxa-1-azabicyclo[3.3.0]oct-3-ene derivatives **13b** (65%) and **13c** (88%).

In the cyclization reactions described above the oxime group acts either as an oxygen or as a nitrogen nucleophile in capturing the seleniranium intermediates. This behaviour is clearly dictated by the geometry of the oxime. In the corresponding intermolecular reactions between an alkene and an oxime this restriction does not exist and the two nucleophilic centres can therefore compete in trapping the cationic intermediates. In order to verify this hypothesis styrene and cyclohexene were allowed to react with the phenylselenenylating agent in the presence of acetone oxime in nitromethane. In both cases the only products observed were those deriving from the trapping of the seleniranium intermediates by the oxygen atom, *i.e.* oximes **14** (63%) and **16** (58%). Only by working in acetonitrile could compound **15** be isolated, although in very low yield (7%).



14 **15** **16**

The course of these reactions is therefore influenced by the experimental conditions employed, and an appropriate choice of the selenenylating agent and of the solvent will hopefully allow the reaction to be directed towards one or the other of the two possible products. Further work on these intermolecular and intramolecular selenium-induced oxime-alkene reactions is currently underway in our laboratory.

Experimental

M.p.s were determined on a Kofler melting-apparatus and are uncorrected. GLC analyses and MS spectra were carried out with an HP 5890 gas chromatograph (dimethyl silicone column, 12.5 m) equipped with an HP 5971 Mass Selective Detector. ^1H and ^{13}C NMR spectra were recorded at 200 and 50.32 MHz, respectively, on a Bruker AC 200 instrument; $CDCl_3$ was used as solvent and $SiMe_4$ as standard. All *J*-values are in Hz. Elemental analyses were carried out on a Carlo Erba 1106 Elemental Analyzer. Light petroleum refers to the fraction boiling in the range 40–60 °C.

Preparation of the Oximes **1a–c** *and* **2**.—Hex-5-en-2-one, acetone oxime and cyclopentanone oxime were commercial products. Acetophenone oxime was prepared from acetophenone by standard methods. 1-Phenylpent-4-en-1-one was prepared as described in the literature.[12] The oximes were prepared according to the two following general methods. The configurations were assigned on the basis of their ^{13}C spectra.[13]

Method A. To 7.5 mol dm^{-3} aq. sodium hydroxide (20 cm^3) were added hydroxylamine hydrochloride (22 mmol) and the ketone (20 mmol) and the resulting mixture was stirred at 50 °C for 15–20 h. The mixture was diluted with water and extracted with methylene dichloride. The organic layer was washed with water, dried ($NaSO_4$), and evaporated. Reaction yields are reported in Table 1. They were calculated on isolated products after column chromatography through a silica gel column with a 1:10 mixture of diethyl ether and light petroleum as eluent. Physical and spectral data are reported below.

1-*Phenylpent-4-en-1-one oxime* **1a**. (E)-*Isomer:* m.p. 55–56 °C; δ_H 9.2 (1 H, br s), 7.65–7.57 (2 H, m), 7.42–7.38 (3 H, m), 5.86 (1 H, ddt, *J* 6.6, 10.1 and 16.8), 5.12–4.93 (2 H, m), 2.92 (2 H, dd, *J* 7.2 and 9.5) and 2.45–2.25 (2 H, m); δ_C 159.2, 137.4, 135.7, 129.2, 128.6, 126.4, 115.2, 30.3 and 25.7; *m/z* 175 (M^+, 67%), 174 (94), 158 (34), 143 (43), 128 (25), 117 (28), 104 (94), 103 (37), 91 (36), 77 (100), 55 (60) and 51 (35) (Found: C, 75.3; H, 7.6; N, 8.1. $C_{11}H_{13}NO$ requires C, 75.40; H, 7.48; N, 7.99%); (Z)-*isomer:* m.p. 48–49 °C; δ_H 9.41 (1 H, br s), 7.48–7.3 (5 H, m), 5.78 (1 H, ddt, *J* 6.4, 9.6 and 11.0), 5.03–4.92 (2 H, m), 2.62 (2 H, dd, *J* 7.2 and 9.5) and 2.28–2.13 (2 H, m); δ_C 157.8, 137.0, 133.3, 128.8, 128.2, 127.8, 115.4, 34.7 and 30.5; *m/z* 175 (M^+, 48%), 174 (100), 158 (36), 143 (41), 128 (25), 117 (23), 104 (96), 103 (34), 91 (32), 77 (75), 55 (52) and 51 (27) (Found: C, 75.45; H, 7.55; N, 7.9%)

(Z)- *and* (E)-*Hex-5-en-2-one oxime* **1b**. Spectra of (Z)- and (E)-*isomers* were attributed according to their relative abundance. (E)-*isomer:* $\delta_H(C_6D_6)$ 10.45 (1 H, br s), 5.82–5.58 (1 H, m), 5.05–4.95 (2 H, m), 2.15–2.0 (4 H, m) and 1.71 (3 H, s); δ_C 157.7, 137.2, 115.2, 35.1, 30.4 and 13.5; *m/z* 113 (M^+, 15%), 112 (16), 98 (85), 96 (57), 81 (55), 55 (100), 54 (41), 42 (90) and 41 (61); (Z)-*isomer:* $\delta_H(C_6D_6)$ 10.45 (1 H, br s), 5.82–5.58 (1 H, m), 4.95–4.8 (2 H, m), 2.4 (2 H, dd, *J* 7.4 and 9.4), 2.15–2.0 (2 H, m) and 1.61 (3 H, s); δ_C 158.0, 137.4, 115.1, 29.3, 27.9 and 19.8; *m/z* 113 (M^+, 2.5%), 112 (6), 98 (21), 96 (16), 94 (16), 81 (21), 58 (12), 55 (56), 54 (100), 42 (48) and 41 (38) (Found: C, 63.6; H, 9.7; N, 12.5. $C_6H_{11}NO$ requires C, 63.69; H, 9.80; N, 12.38%).

Method B. In this case the desired products were obtained by allylation or benzylation of the dianion of the appropriate oximes according to the general procedure described in the literature.[7] The reactions were carried out on 20 mmol of the oxime. Details are given in the Results and Discussion section. Reaction yields were calculated on isolated products after column chromatography and are reported in Table 1. Compounds **1a** and **1b** have been described above. Physical and spectral data of the other oximes are reported below.

(Z)- *and* (E)-1-*Phenylhept-6-en-3-one oxime* **1c**. δ_H 9.55 (1 H, br s), 7.33–7.0 (5 H, m), 5.95–5.55 (1 H, m), 5.12–4.85 (2 H, m) and 2.95–2.05 (8 H, m); δ_C 160.15, 160.1, 141.3, 141.2, 137.4, 137.3, 135.7, 128.9, 128.4, 128.2, 126.0, 116.5, 115.2, 36.1, 33.8, 32.6, 31.5, 30.1, 30.0, 29.5 and 27.3; *m/z* 203 (M^+, 3.6%), 202 (3), 162 (91), 112 (18), 91 (100), 77 (12), 42 (13) and 41 (12); 203 (M^+, 7.1%), 202 (3), 186 (15), 105 (19), 104 (35), 91 (100), 77 (11), 55 (19) and 41 (10) (Found: C, 76.9; H, 8.5; N, 6.8. $C_{13}H_{17}NO$ requires C, 76.81; H, 8.43; N, 6.89%).

2-*Allylcyclopentanone oxime* **2**. (E)-*Isomer:* δ_H 9.3 (1 H, br s), 5.80 (1 H, ddt, *J* 6.7, 10.1 and 17.0), 5.12–4.95 (2 H, m), 2.71–2.30 (4 H, m) and 2.23–1.25 (5 H, m); δ_C 168.1, 136.3, 116.1, 42.6, 36.4, 31.1, 27.3 and 22.3; *m/z* 139 (M^+, 37.4%), 138 (40), 122 (57), 111 (21), 105 (21), 98 (21), 97 (27), 96 (33), 95 (43), 94 (27), 81 (37), 80 (72), 79 (100), 67 (53), 55 (35), 54 (33), 53 (88) and 41 (89) (Found: C, 68.9; H, 9.5; N, 10.1. $C_8H_{13}NO$ requires C, 69.03; H, 9.41; N, 10.06%); (Z)-*isomer:* δ_H 9.55 (1 H, br s), 5.77 (1 H, ddt, *J* 6.8, 9.7 and 16.9), 5.12–4.97 (2 H, m), 3.10–2.95 (1 H, m), 2.73–2.58 (1 H, m), 2.42–2.30 (2 H, m), 2.28–2.05 (1 H, m) and 1.93–1.55 (4 H, m); δ_C 168.2, 136.5, 116.2, 39.0, 34.6, 31.0, 30.0 and 23.0; *m/z* 139 (M^+, 34.9%), 138 (52), 122 (56), 111 (22), 105 (20), 98 (22), 97 (27), 96 (38), 95 (44), 94 (33), 81 (49), 80 (81), 79 (100), 67 (63), 55 (41), 54 (36), 53 (93) and 41 (95) (Found: C, 69.1; H, 9.3; N, 10.2%).

Selenium-induced Cyclizations. General Procedure.—To a mixture of diphenyl diselenide (2.5 mmol) and ammonium persulfate (5 mmol) in acetonitrile (10 cm^3) was added trifluoromethanesulfonic acid (5 mmol) dropwise. To the resulting deep red solution was added the γ-alkenyl oxime (5 mmol) in small portions. The almost colourless mixture was stirred at room temperature for 1–2 h and was then poured onto

water–methylene dichloride. The organic layer was washed with water, dried ($NaSO_4$), and evaporated. The residue was chromatographed through a silica gel column with a 96:4 mixture of methylene dichloride and methanol as eluent. The reaction products obtained and the reaction yields are summarized in Scheme 2 and Table 2. Physical and spectral data are reported below.

5,6-*Dihydro*-3-*phenyl*-6-[(*phenylseleno*)*methyl*]-4H-1,2-*oxazine* **3a**. δ_H 7.7–7.6 (2 H, m), 7.6–7.49 (2 H, m), 7.4–7.3 (3 H, m), 7.3–7.2 (3 H, m), 3.91 (1 H, dddd, *J* 2.3, 5.1, 7.8 and 12.9), 3.34 (1 H, dd, *J* 5.1 and 12.7), 2.99 (1 H, dd, *J* 7.8 and 12.7), 2.77–2.45 (2 H, m), 2.41–2.21 (1 H, m) and 1.95–1.65 (1 H, m); δ_C 154.6, 135.5, 132.6, 129.4, 129.1, 128.4, 127.1, 125.3, 74.4, 30.4, 23.9 and 21.7; *m*/*z* 331 (M^+, 15.2%), 238 (39), 174 (45), 157 (37), 156 (63), 91 (59), 77 (100), 55 (32) and 51 (30) (Found: C, 61.6; H, 5.25; N, 4.3. $C_{17}H_{17}NOSe$ requires C, 61.82; H, 5.19; N, 4.24%).

5,6-*Dihydro*-3-*methyl*-6-[(*phenylseleno*)*methyl*]-4H-1,2-*oxazine* **3b**. M.p. 33–35 °C; δ_H 7.55–7.45 (2 H, m), 7.30–7.15 (3 H, m), 3.81–3.61 (1 H, m), 3.21 (1 H, dd, *J* 5.1 and 12.5), 2.95 (1 H, dd, *J* 7.6 and 12.5), 2.25–1.90 (3 H, m), 1.85 (3 H, s) and 1.8–1.5 (1 H, m); δ_C 155.2, 132.0, 129.7, 128.7, 126.6, 73.1, 30.2, 24.4, 23.6 and 21.1; *m*/*z* 269 (M^+, 33.8%), 176 (28), 157 (30), 112 (100), 91 (78), 77 (37), 55 (38) and 41 (60) (Found: C, 53.9; H, 5.8; N, 5.3. $C_{12}H_{15}NOSe$ requires C, 53.74; H, 5.64; N, 5.22%).

5,6-*Dihydro*-3-*phenethyl*-6-[(*phenylseleno*)*methyl*]-4H-1,2-*oxazine* **3c**. M.p. 80–82 °C; δ_H 7.60–7.45 (2 H, m), 7.32–7.10 (8 H, m), 3.82–3.68 (1 H, m), 3.22 (1 H, dd, *J* 5.1 and 12.7), 2.89 (1 H, dd, *J* 8.1 and 12.7), 2.90–2.80 (2 H, m), 2.56–2.42 (2 H, m), 2.20–2.0 (3 H, m) and 1.79–1.51 (1 H, m); δ_C 157.8, 140.9, 132.5, 129.9, 129.1, 128.4, 128.2, 127.0, 126.1, 73.8, 37.2, 32.6, 30.5, 23.8 and 23.7; *m*/*z* 359 (M^+, 11.9%), 266 (14), 202 (40), 188 (15), 184 (28), 157 (21), 105 (67), 91 (100) and 77 (26) (Found: C, 63.5; H, 5.8; N, 4.0. $C_{19}H_{21}NOSe$ requires C, 63.69; H, 5.91; N, 3.91%).

3,4,4a,5,6,7-*Hexahydro*-3-[(*phenylseleno*)*methyl*]*cyclopenta*-[c]-1,2-*oxazine* **5**. δ_H 7.60–7.48 (2 H, m), 7.32–7.20 (3 H, m), 4.0–3.72 (1 H, m), 3.31 (1 H, dd, *J* 4.8 and 12.6), 2.95 (1 H, dd, *J* 8.0 and 12.6), 2.60–2.0 (5 H, m), 1.99–1.50 (2 H, m) and 1.40–1.10 (2 H, m); δ_C 164.0, 132.4, 130.0, 129.1, 127.0, 73.4, 36.8, 31.5, 30.8, 29.5, 28.8 and 21.4; *m*/*z* 200 (M^+ − 95, 98.0%), 171 (64), 157 (56), 91 (100), 77 (37) and 51 (23) (Found: C, 57.1; H, 5.9; N, 4.9. $C_{14}H_{17}NOSe$ requires C, 57.15; H, 5.82; N, 4.76%).

3,4-*Dihydro*-5-*phenyl*-2-[(*phenylseleno*)*methyl*]-2H-*pyrrole* 1-*oxide* **4a**. δ_H 8.4–8.25 (2 H, m), 7.6–7.48 (2 H, m), 7.48–7.32 (3 H, m), 7.3–7.15 (3 H, m), 4.52–4.35 (1 H, m), 3.69 (1 H, dd, *J* 3.7 and 12.7), 3.28 (1 H, dd, *J* 8.3 and 12.7), 3.12–2.98 (2 H, m), 2.37 (1 H, ddt, *J* 5.4, 8.3 and 13.5) and 2.01 (1 H, ddt, *J* 6.6, 9.3 and 13.5); δ_C 139.4, 132.2, 129.8, 129.1, 128.8, 127.9, 126.9, 126.8, 74.3, 30.0, 28.3 and 22.4; *m*/*z* 331 (M^+, 14.5%), 315 (21), 238 (78), 220 (66), 174 (42), 158 (55), 157 (43), 156 (89), 144 (100), 115 (51), 104 (82), 91 (77), 77 (82) and 55 (50) (Found: C, 61.9; H, 5.3; N, 4.4. $C_{17}H_{17}NOSe$ requires C, 61.82; H, 5.29; N, 4.24%).

3,4-*Dihydro*-5-*methyl*-2-[(*phenylseleno*)*methyl*]-2H-*pyrrole* 1-*oxide* **4b**. δ_H 7.58–7.45 (2 H, m,), 7.3–7.1 (3 H, m), 4.35–4.2 (1 H, m), 3.54 (1 H, dd, *J* 3.6 and 12.8), 3.22 (1 H, dd, *J* 8.0 and 12.8), 2.70–2.55 (2 H, m), 2.28 (1 H, ddt, *J* 5.8, 8.5 and 13.5), 1.98 (3 H, d, *J* 1.4) and 1.90 (1 H, ddt, *J* 6.4, 9.0 and 13.5); δ_C 143.8, 132.4, 129.1, 129.0, 127.0, 71.7, 30.8, 30.0, 22.8 and 12.5; *m*/*z* 269 (M^+, 11.9%), 176 (50), 174 (27), 157 (20), 112 (100), 94 (41), 77 (34), 55 (46) and 51 (22) (Found: C, 53.65; H, 5.8; N, 5.15. $C_{12}H_{15}NOSe$ requires C, 53.74; H, 5.64; N, 5.22%).

3,4-*Dihydro*-5-*phenethyl*-2-[(*phenylseleno*)*methyl*]-2H-*pyrrole* 1-*oxide* **4c**. M.p. 93–95 °C; δ_H 7.60–7.48 (2 H, m), 7.35–7.10 (8 H, m), 4.35–4.15 (1 H, m), 3.59 (1 H, dd, *J* 3.6 and 12.7), 3.19 (1 H, dd, *J* 8.1 and 12.7), 2.95–2.63 (4 H, m), 2.60–2.38 (2 H, m), 2.18 (1 H, ddt, *J* 5.8, 8.2 and 12.6) and 1.79 (1 H, ddt, *J* 5.9, 9.0 and 12.6); δ_C 146.8, 140.0, 132.2, 129.2, 128.9, 128.2, 127.9, 126.9, 126.0, 71.9, 30.2, 29.8, 29.4, 27.8 and 22.8; *m*/*z* 343 (M^+ − 16, 26.0%), 262 (23), 248 (43), 172 (47), 157 (11), 105 (18), 91 (100), 77 (13) and 55 (13) (Found: C, 63.5; H, 6.0; N, 4.0. $C_{19}H_{21}NOSe$ requires C, 63.69; H, 5.91; N, 3.91%).

2,3,3a,4,5,6-*Hexahydro*-2-[(*phenylseleno*)*methyl*]*cyclopenta*-[b]*pyrrole* 1-*oxide* **6**. δ_H 7.60–7.40 (2 H, m), 7.30–7.12 (3 H, m), 4.60–4.40 (1 H, m), 3.5 (1 H, dd, *J* 3.6 and 12.6), 3.35 (1 H, dd, *J* 8.2 and 12.6), 3.4–3.2 (1 H, m) and 2.6–1.9 (8 H, m); δ_C 155.5, 136.2, 129.2, 128.7, 62.1, 42.6, 33.7, 32.5, 32.2, 28.4 and 21.7; *m*/*z* 279 (M^+ − 16, 30.1%), 198 (38), 184 (20), 157 (11), 122 (100), 108 (10), 105 (22), 95 (55), 81 (22), 77 (27), 67 (42) and 55 (15) (Found: C, 57.3; H, 5.9; N, 4.6. $C_{14}H_{17}NOSe$ requires C, 57.15; H, 5.82; N, 4.76%).

Preparation of Derivatives of 1,2-*Oxazines and of Cyclic Nitrones*.—As indicated in structures **14**–**16**, several derivatives of the 1,2-oxazines and of the cyclic nitrones were prepared. The reductions of substrates **3a**, **3b**, **8a** and **4b** were carried out with sodium cyanoborohydride according to the procedure described in the literature.[14] The deselenenylation of compound **3a** was effected with Raney Ni in ethanol at room temperature. The deoxygenations were effected with phosphorus trichloride in refluxing benzene in the case of compound **4a** and at room temperature in the case of compound **4b**. The cycloadditions of compounds **4b** and **4c** with methyl propiolate were effected at room temperature according to the procedure reported in the literature.[11] In every case the progress of the reaction was monitored by TLC and GC-MS. The reaction mixtures were worked up in the usual way and the reaction products were purified by column chromatography. Reaction yields are indicated in the Results and Discussion section. Physical and spectral data are reported below.

3,4,5,6-*Tetrahydro*-3-*phenyl*-6-[(*phenylseleno*)*methyl*]-2H-1,2-*oxazine* **7a**. M.p. 73–74 °C; $\delta_H(C_6D_6)$ 7.59–7.42 (2 H, m), 7.29–6.91 (8 H, m), 5.32 (1 H, br s), 3.95 (1 H, ddt, *J* 2.0, 6.3 and 10.6), 3.85–3.70 (1 H, m), 3.08 (1 H, dd, *J* 6.4 and 12.4), 2.77 (1 H, dd, *J* 6.2 and 12.4), 1.72–1.58 (3 H, m) and 1.42–1.18 (1 H, m); δ_C 139.8, 132.4, 130.4, 129.0, 128.4, 127.8, 127.2, 126.7, 78.2, 62.2, 31.5, 31.3 and 30.9; *m*/*z* 333 (M^+, 1.4%), 176 (6), 157 (7), 122 (100), 117 (14), 106 (18), 91 (48), 77 (18) and 55 (6) (Found: C, 61.35; H, 5.8; N, 4.2. $C_{17}H_{19}NOSe$ requires C, 61.45; H, 5.76; N, 4.22%).

3,4,5,6-*Tetrahydro*-3-*methyl*-6-[(*phenylseleno*)*methyl*]-2H-1,2-*oxazine* **7b**. δ_H 7.57–7.42 (2 H, m), 7.31–7.12 (3 H, m), 4.82 (1 H, br s), 3.79–3.61 (1 H, m), 3.2–3.0 (1 H, m), 3.05 (1 H, dd, *J* 6.5 and 12.4), 2.85 (1 H, dd, *J* 6.2 and 12.4), 1.95–1.70 (2 H, m), 1.55–1.10 (2 H, m) and 0.95 (3 H, d, *J* 6.5); δ_C 132.2, 130.3, 128.8, 126.6, 78.5, 52.6, 31.9, 31.2, 30.5 and 17.7; *m*/*z* 271 (M^+, 2.7%), 157 (7), 114 (17), 91 (8), 77 (7), 60 (100) and 55 (16) (Found: C, 53.2; H, 6.45; N, 5.1. $C_{12}H_{17}NOSe$ requires C, 53.34; H, 6.34; N, 5.18%).

3,4,5,6-*Tetrahydro*-6-*methyl*-3-*phenyl*-2H-1,2-*oxazine* **9a**. δ_H 7.4–7.2 (5 H, m), 5.1 (1 H, br s), 4.02 (1 H, dd, *J* 3.7 and 10.1), 3.86 (1 H, ddq, *J* 2.2, 6.3 and 10.8), 2.0–1.75 (3 H, m), 1.6–1.4 (1 H, m) and 1.19 (3 H, d, *J* 6.3); δ_C 140.2, 128.4, 127.8, 127.3, 75.2, 62.2, 32.9, 31.7 and 20.1; *m*/*z* 177 (M^+, 46.3%), 162 (22), 145 (15), 132 (36), 122 (86), 121 (41), 120 (40), 104 (100), 91 (58), 77 (54), 60 (37) and 51 (24) (Found: C, 74.6; H, 8.6; N, 7.8. $C_{11}H_{15}NO$ requires C, 74.54; H, 8.53; N, 7.90%).

2-*Methyl*-5-[(*phenylseleno*)*methyl*]*pyrrolidin*-1-*ol* **11b**. trans-*Isomer:* m.p. 97–99 °C; δ_H 7.52–7.41 (2 H, m), 7.23–7.10 (3 H, m), 6.4–5.6 (1 H, m), 3.33–3.20 (1 H, m), 3.11–2.95 (2 H, m), 2.90–2.70 (1 H, m), 2.01–1.73 (2 H, m), 1.60–1.20 (2 H, m) and 1.18 (3 H, d, *J* 6.1); δ_C 132.0, 130.5, 128.9, 126.5, 67.5, 63.7, 31.7, 27.1, 25.7 and 18.6 (Found: C, 53.2; H, 6.4; N, 5.3. $C_{12}H_{17}NOSe$ requires C, 53.34; H, 6.34; N, 5.18%); cis-*isomer:* δ_H 8.45–7.95 (1 H, m), 7.52–7.40 (2 H, m), 7.28–7.10 (3 H, m), 3.50–3.20 (3 H, m), 2.90–2.72 (1 H, m), 2.10–1.81 (2 H, m), 1.68–1.21 (2 H, m) and 1.11 (3 H, d, *J* 6.6); δ_C 131.9, 130.4, 128.8, 126.4,

65.2, 61.1, 29.6, 28.2, 26.9 and 16.7 (Found: C, 53.3; H, 6.2; N, 5.1%).

These were converted into the acetyl derivative **12b** by reaction with acetic anhydride in pyridine. Trans-*isomer*: δ_H 7.5–7.4 (2 H, m), 7.28–7.15 (3 H, m), 3.3–2.89 (4 H, m), 2.06 (3 H, s), 2.05–1.75 (2 H, m), 1.65–1.38 (2 H, m) and 1.12 (3 H, d, *J* 6.1); δ_C 170.0, 131.8, 129.8, 128.5, 126.3, 66.5, 62.7, 30.3, 26.5, 25.7, 19.0 and 17.6 (Found: C, 54.2; H, 6.5; N, 4.7. $C_{14}H_{19}NO_2Se$ requires C, 53.85; H, 6.13; N, 4.49%); cis-*isomer*: δ_H 7.60–7.42 (2 H, m), 7.30–7.15 (3 H, m), 3.69–3.50 (2 H, m), 3.27 (1 H, dd, *J* 4.9 and 11.9), 2.88 (1 H, dd, *J* 5.2 and 11.9), 2.21–1.93 (2 H, m), 2.05 (3 H, s), 1.72–1.42 (2 H, m) and 1.12 (3 H, d, *J* 6.6); δ_C 169.8, 132.4, 130.2, 129.0, 126.8, 65.4, 61.2, 30.2, 29.0, 27.7, 19.4 and 16.5 (Found: C, 53.5; H, 6.6; N, 4.2.

5,6-*Dihydro*-6-*methyl*-3-*phenyl*-4H-1,2-*oxazine* **8a**. δ_H 7.78–7.63 (2 H, m), 7.4–7.32 (3 H, m), 3.88 (1 H, ddq, *J* 2.2, 6.2 and 10.3), 2.70–2.58 (2 H, m), 2.13–1.98 (1 H, m), 1.85–1.65 (1 H, m) and 1.41 (3 H, d, *J* 6.2); δ_C 154.2, 136.0, 129.3, 128.3, 125.2, 71.2, 26.2, 22.0 and 19.7; *m/z* 175 (M^+, 100%), 160 (17), 130 (85), 103 (95), 91 (25), 77 (93), 55 (11) and 51 (36) (Found: C, 75.3; H, 7.3; N, 8.1. $C_{11}H_{13}NO$ requires C, 75.40; H, 7.48; N, 7.99%).

3,4-*Dihydro*-5-*phenyl*-2-[(*phenylseleno*)*methyl*]-2H-*pyrrole* **10a**. δ_H 7.88–7.77 (2 H, m), 7.6–7.5 (2 H, m), 7.48–7.32 (3 H, m), 7.3–7.18 (3 H, m), 4.6–4.42 (1 H, m), 3.48 (1 H, dd, *J* 4.7 and 12.0), 3.18–2.8 (2 H, m), 3.09 (1 H, dd, *J* 8.0 and 12.0), 2.4–2.18 (1 H, m) and 1.9–1.7 (1 H, m); δ_C 173.3, 134.4, 132.6, 130.6, 129.0, 128.4, 127.8, 126.8, 73.0, 35.4, 34.4 and 28.6; *m/z* 315 (M^+, 40.7%), 234 (55), 220 (100), 157 (15), 144 (94), 104 (48), 91 (58), 77 (31) and 55 (21) (Found: C, 65.05; H, 5.6; N, 4.3. $C_{17}H_{17}NSe$ requires C, 64.97; H, 5.45; N, 4.46%).

3,4-*Dihydro*-5-*methyl*-2-[(*phenylseleno*)*methyl*]-2H-*pyrrole* **10b**. δ_H 7.61–7.43 (2 H, m), 7.31–7.12 (3 H, m), 4.32–4.12 (1 H, m), 3.32 (1 H, dd, *J* 5.2 and 12.0), 2.97 (1 H, dd, *J* 7.0 and 12.0), 2.68–2.31 (2 H, m), 2.21–2.01 (1 H, m), 2.0 (3 H, s) and 1.7–1.5 (1 H, m); δ_C 175.4, 132.3, 128.9, 126.6, 72.4, 39.2, 34.2, 29.0 and 19.6; *m/z* 253 (M^+, 26.5%), 172 (38), 158 (100), 157 (15), 91 (18), 82 (18), 77 (17), 55 (50), 51 (12) and 42 (38) (Found: C, 57.3; H, 6.1; N, 5.7. $C_{12}H_{15}NSe$ requires C, 57.15; H, 5.99; N, 5.55%).

Methyl 5-*methyl*-8-[(*phenylseleno*)*methyl*]-2-*oxa*-1-*azabicyclo*[3.3.0]*oct*-3-*ene*-4-*carboxylate* **13b**. δ_H 7.52–7.40 (2 H, m), 7.28–7.17 (4 H, m), 3.7 (3 H, s), 3.50–3.22 (2 H, m), 2.9 (1 H, dd, *J* 8.3 and 12.0), 2.30–2.10 (1 H, m), 2.08–1.88 (2 H, m), 1.70–1.51 (1 H, m) and 1.43 (3 H, s); δ_C 163.8, 152.0, 132.1, 130.2, 128.9, 126.6, 113.3, 74.1, 70.8, 50.8, 35.7, 30.5, 27.4 (CH_2) and 27.4 (Me); *m/z* 335 (M^+ − 18, 35.8%), 276 (7), 178 (16), 164 (100), 157 (4), 146 (20), 132 (18), 118 (27), 106 (13), 104 (14), 91 (11), 78 (13) and 77 (10) (Found: C, 54.6; H, 5.55; N, 4.1. $C_{16}H_{19}NO_3Se$ requires C, 54.55; H, 5.44; N, 3.98%).

Methyl 5-*phenethyl*-8-[(*phenylseleno*)*methyl*]-2-*oxa*-1-*azabicyclo*[3.3.0]*oct*-3-*ene*-4-*carboxylate* **13c**. δ_H 7.55–7.42 (2 H, m), 7.30–7.05 (9 H, m), 3.68 (3 H, s), 3.51–3.32 (1 H, m), 3.31 (1 H, dd, *J* 4.5 and 12.1), 3.05 (1 H, dd, *J* 8.2 and 12.1), 2.80–2.42 (2 H, m) and 2.30–1.49 (6 H, m); δ_C 163.8, 152.5, 142.0, 132.1, 130.5, 128.9, 128.3, 128.1, 126.7, 125.5, 111.2, 71.1, 51.0, 41.2, 35.5, 30.7, 30.2 and 27.6; *m/z* 425 (M^+ − 18, 22.9%), 366 (6), 254 (100), 208 (11), 194 (11), 157 (4), 91 (48) and 77 (7) (Found: C, 62.3; H, 5.9; N, 3.1. $C_{23}H_{25}NO_3Se$ requires C, 62.44; H, 5.70; N, 3.17%).

Intermolecular Reactions.—To the selenenylating agent, prepared from PhSeSePh (2.5 mmol) as described above in either acetonitrile or nitromethane (see Results and Discussion section), a solution of styrene or cyclohexene (3 mmol) and acetone oxime (15 mmol) was added. The mixture was stirred at room temperature for 1 h. The progress of the reaction was monitored by TLC and by GC-MS. The reaction mixture was worked up in the usual way and the products were isolated by column chromatography. The products obtained were **14–16**. Physical and spectral data are reported below.

2-[1-*Phenyl*-2-(*phenylseleno*)*ethoxyimino*]*propane* **14**. δ_H 7.5–7.15 (10 H, m), 5.29 (1 H, dd, *J* 5.9 and 7.3), 3.46 (1 H, dd, *J* 7.3 and 12.4), 3.23 (1 H, dd, *J* 5.9 and 12.4), 1.87 (3 H, s) and 1.8 (3 H, s); δ_C 155.3, 141.3, 132.3, 130.9, 128.8, 128.2, 127.8, 126.9, 83.5, 33.7, 21.7 and 15.7; *m/z* 333 (M^+, 5.0%), 260 (27), 183 (39), 157 (26), 104 (15), 91 (17), 77 (22), 56 (100) and 51 (11) (Found: C, 61.6; H, 5.6; N, 4.3. $C_{17}H_{19}NOSe$ requires C, 61.45; H, 5.76; N, 4.22%).

N-*Isopropylidene*-1-*phenyl*-2-(*phenylseleno*)*ethylamine* N-*oxide* **15**. δ_H 7.62–7.45 (2 H, m), 7.42–7.1 (8 H, m), 4.75 (1 H, dd, *J* 3.6 and 9.2), 3.3 (1 H, dd, *J* 3.6 and 12.7), 3.12 (1 H, dd, *J* 9.2 and 12.7), 1.85 (3 H, s) and 1.84 (3 H, s); δ_C 156.4, 142.4, 141.4, 133.1, 132.3, 129.2, 128.8, 128.5, 125.8, 72.2, 35.2, 22.0 and 16.1 (Found: C, 61.4; H, 5.6; N, 4.1. $C_{17}H_{19}NOSe$ requires C, 61.45; H, 5.76; N, 4.22%).

2-[2-(*Phenylseleno*)*cyclohexyloxyimino*]*propane* **16**. δ_H 7.6–7.5 (2 H, m), 7.28–7.18 (3 H, m), 4.05 (1 H, dt, *J* 3.8 and 8.4), 3.42 (1 H, dt, *J* 4.2 and 8.4), 2.24–2.0 (2 H, m), 1.88 (3 H, s), 1.81 (3 H, s) and 1.8–1.2 (6 H, m); δ_C 154.3, 134.6, 129.6, 128.6, 127.0, 82.8, 45.8, 31.8, 31.3, 25.4, 23.3, 21.8 and 15.6; *m/z* 311 (M^+, 5.0%), 238 (45), 157 (20), 81 (98), 79 (16), 77 (16), 74 (55), 56 (100) and 41 (20) (Found: C, 58.0; H, 6.9; N, 4.4. $C_{15}H_{21}NOSe$ requires C, 58.06; H, 6.82; N, 4.51%).

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