Elimination Reactions of Terminal β-Oxy Selenoxides. Synthesis of Aryl and Vinyl Enol Ethers and of Furans, Oxazoles, and Thiazoles

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Elimination reactions of terminal selenoxides holding an alkoxy group in the β position, RCH(OR)CH_2SeOPh, are usually difficult and can give rise to complex reaction mixtures. We report that these reactions take place more easily whenever the oxygen atom is linked to an unsaturated group (—CH=CHR, —Ar, —CR=O, —CH=NR). These selenoxides are easily available, and the elimination reaction was employed to effect useful syntheses of both open-chain and cyclic aryl and vinyl enol ethers. Moreover, by simple isomerization with acids or bases the cyclic derivatives can be transformed into the corresponding furans. The same procedure has been employed to synthesize substituted oxazoles and thiazoles also.

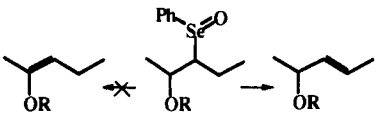
Introduction

Most selenoxides are thermally unstable and easily give rise to stereospecific syn elimination of selenenic acid to afford alkenes.[1] In the case of internal β-oxy selenoxides the reaction is also regiospecific, the elimination occurring selectively away from the carbon atom holding the oxygen atom (Scheme I). This reaction is therefore very useful for the preparation of allylic alcohols, ethers and esters.[1]

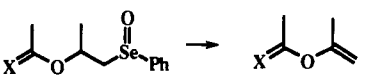
The most satisfactory explanation for this interesting and useful course of the syn elimination reaction assumes an antiparallel orientation of the selenoxide and the oxygen lone electron pairs.[2] As a matter of fact, the terminal β-oxy selenoxides, RCH(OR)CH_2SeOPh, in which the elimination can only proceed by abstraction of the hydrogen atom linked to the carbon holding the oxygen-containing function, are stable and isolable compounds.[3] Nevertheless, several examples of the elimination reaction of this kind of selenoxides are reported in the literature. In every case, however, the elimination requires forced reaction conditions and the use of an organic base. Moreover, other compounds are usually formed together with the desired elimination product.[4]

On the basis of the above-reported interpretation of the factors effecting the regioselectivity of the elimination reaction of internal β-oxy selenoxides,[2] it can be suggested that in the case of a terminal β-oxy selenoxide the elimination reaction might become easier by decreasing the electron density on the oxygen atom. Indeed, Engman has recently reported that vinyl acetates can be easily obtained from the elimination of selenoxides derived from the acetoxy selenenylation of terminal alkenes.[4] In order to verify the validity of this hypothesis selenoxides having the general structure reported in Scheme II, in which the oxygen atom is linked to a carbon–carbon, carbon–oxygen, or carbon–nitrogen double bond, have been synthesized.

Scheme I



Scheme II



X = CHR, O, NR

We report in this paper that these kinds of terminal selenoxides easily give rise to the corresponding elimination products as indicated in Scheme II. The results obtained, beside supporting the above-reported hypothesis about the factors governing the selenoxide elimination reaction, also have synthetic relevance since this reaction can be used to easily prepare different types of organic compounds. The results which will be described below concern the synthesis of open-chain and cyclic aryl and vinyl enol ethers, the synthesis of substituted furans, aryl oxazoles, and thiazoles and of γ-methylene γ-lactones.

Results and Discussion

The selenoxides employed for the present investigation were prepared by oxidation of the selenides 1–8 (Chart I). These substrates were selected in order to have examples of compounds in which the oxygen atom in the β position is linked to an aromatic ring (1 and 5) and to carbon–carbon (2, 3, and 4), carbon–nitrogen (6), and carbon–oxygen (8) double bonds. Also investigated were some sulfur derivatives (7). All these selenides were easily obtained, according to our recently introduced procedure,[5] from the reaction of alkenes with the strongly electrophilic phenylselenenyl sulfate (generated in situ by the oxidation of diphenyl diselenide with ammonium peroxydisulfate).

The β-(phenylseleno)alkyl aryl ethers 1 were obtained from the phenylselenenylation of 1-octene, in nitromethane, in the presence of *p*-methyl- and *p*-nitrophenol. The β-(phenylseleno)alkyl vinyl ethers 2 were obtained from the addition of β-hydroxy phenylselenides (prepared from

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(3) Tiecco, M.; Chianelli, D.; Tingoli, M.; Testaferri, L.; Bartoli, D. *Tetrahedron* **1986**, *42*, 4897. Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Bartoli, D. *Tetrahedron* **1988**, *44*, 2261.

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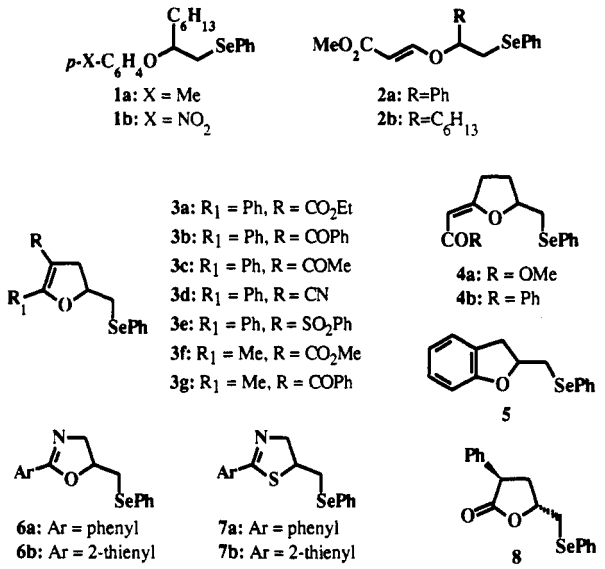
0022-3263/93/1958-1349$04.00/0

Chart I



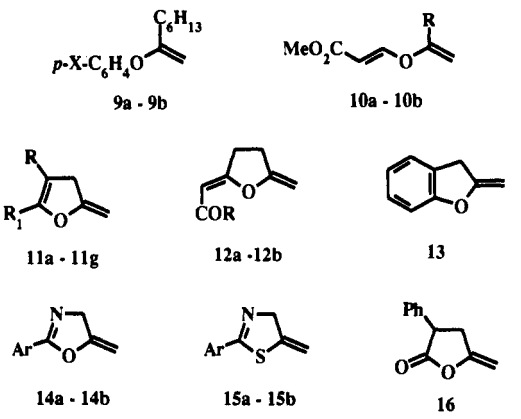
the phenylselenenylation of styrene and 1-octene in water) to methyl propiolate. The cyclic ethers **3–8** were prepared by selenium-induced ring closure reactions.[6,7] Compounds **3** were produced from α-allyl β-keto esters, β-diketones, β-keto nitriles, and β-keto sulfones. Compounds **4** were instead obtained from the products of kynetic allylation of the bis anions of methyl acetoacetate and 1-benzoylacetone. *o*-Allylphenol, *N*-allylamides, and *N*-allylthioamides gave the products **5**, **6**, and **7**, respectively. The *trans*-γ-lactone **8** was prepared from 2-phenyl-4-pentenonitrile.

All these selenides were easily oxidized to the corresponding selenoxides with hydrogen peroxide in methanol at room temperature. TLC and proton NMR analysis of the residues obtained after removal of the solvent under reduced pressure showed the presence of two diastereoisomeric selenoxides which could not be separated because of the facile interconversion of the selenoxide chiral center.[3,8] The products obtained were sufficiently pure to be directly used for the elimination reactions. After several exploratory experiments we found that the best way to effect the elimination reaction was to reflux the crude selenoxides in a mixture of benzene and 10% sodium bicarbonate.[9] After the usual workup the elimination products were purified by column chromatography on silica gel. The products obtained are indicated in Chart II. Reaction conditions and reaction yields are reported in Table I.

Reaction yields are satisfactory in every case, and the products can be easily obtained in a pure form. Only in the case of the selenoxide of **5**, compound **13** was isolated in poor yield because of its facile isomerization to 2-methylbenzofuran (**19**). The ready formation of compounds **15a** and **15b** indicates that the oxidation of the selenium atom and the elimination of the selenoxide function take place easily in the presence of a sulfur atom also.

Although in most cases the elimination reaction of the selenoxides deriving from compounds **1–8** requires long

Chart II



reaction times, the experimental conditions here employed are considerably milder than those necessary in the case of terminal β-alkoxy selenoxides.[4] This clearly supports the hypothesis that the presence of an unsaturated group linked to the oxygen atom facilitates the elimination process.[10]

The 4,5-dihydro-5-methylenefuran derivates **11** can also be obtained by dehydroiodination of the corresponding 4,5-dihydro-5-(iodomethyl)furans[11,12] or by ring closure reactions of α-propargyl β-keto esters.[13] The presently described procedure represents a convenient synthetic route for these compounds with several advantages over the other methods.

Owing to their enolic structure the elimination products **9–15** can certainly find several useful synthetic applications. Moreover, the cyclic derivatives **11–15** are the methylene derivatives of dihydrofuran, dihydrooxazole, and dihydrothiazole and can be easily isomerized into the corresponding aromatic compounds **17–21** (Chart III). This reaction was carried out by simply treating a benzene solution of the exo methylenic compounds either with Amberlist or with DBU[11,12] at room temperature or at 50 °C, respectively, for a few hours. In view of the easy isomerization of **13**, the 2-methylbenzofuran (**19**) was prepared by directly refluxing the solution of the selenoxide **5** in benzene in the presence of DBU. Reaction conditions and reaction yields are reported in Table I.

As indicated in Table I, 5-methyl derivatives of 2,3-substituted and of 2-substituted furans **17a–17g** and **18a,b**, 2-phenyl- and 2-(2′-thienyl)-5-methyloxazole (**20a**, **20b**), and 2-phenyl- and 2-(2′-thienyl)-5-methylthiazole (**21a**, **21b**) (Chart III) were all obtained in good to high yields.

Thus, using the reaction sequence indicated in Scheme III it is possible to build up a 2-substituted 5-methylfuran, -oxazole, or -thiazole nucleus. The synthesis of other heterocyclic compounds can also be easily envisaged. The starting allyl derivatives are readily available and all the reactions occur in good yield and under very simple reaction conditions. For these reasons the presently described procedure represents a general method which conveniently compares with those reported in the liter-

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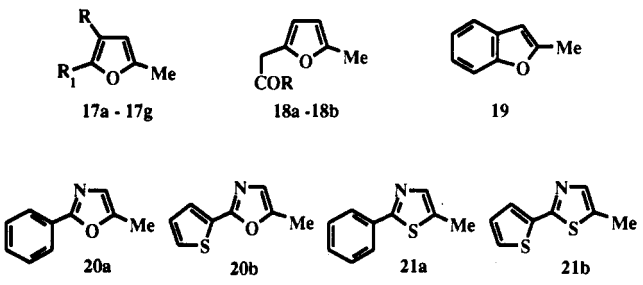
(8) Tiecco, M.; Tingoli, M.; Testaferri, L.; Bartoli, D. *Tetrahedron Lett.* **1987**, *28*, 3849.
(9) Engman, L. *Tetrahedron Lett.* **1987**, *28*, 1463.
(10) Examples of the elimination reaction of β-(aryloxy)selenoxides, similar to those deriving from **1** and **5**, have recently been reported: Williams, R. M.; Cushing, T. D. *Tetrahedron Lett.* **1990**, *31*, 6325.
(11) Antonioletti, B.; Bonadies, F.; Scettri, A. *Tetrahedron Lett.* **1988**, *29*, 4987.
(12) Lee, J. W.; Oh, D. Y. *Heterocycles* **1990**, *31*, 1417.
(13) Couffignal, R. *Synthesis* **1978**, 581 and references cited therein.

Table I

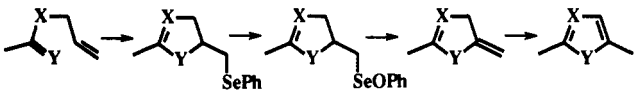
entry	selenide	time,[a] h	time,[b] h	elimination product	yield,[c] %	method[d]	time, h	aromatic compd	yield,[c] %
1	**1a**	1	7	**9a**	52				
2	**1b**	5	3	**9b**	67				
3	**2a**	5	2	**10a**	93				
4	**2b**	5	15	**10b**	67				
5	**3a**	19	6	**11a**	71	A	4	**17a**	71
6	**3b**	3	3	**11b**	54	A	4	**17b**	56
7	**3c**	4	17	**11c**	58	B	4	**17c**	76
8	**3d**	3	15	**11d**	80	A	4	**17d**	75
9	**3e**	4	7	**11e**	67	A	3	**17e**	90
10	**3f**	6	16	**11f**	50	A	3	**17f**	65
11	**3g**	5	20	**11g**	48	B	4	**17g**	76
12	**4a**	5	16	**12a**	81	A	3	**18a**	66
13	**4b**	6	2.5	**12b**	65	B	2.5	**18b**	65
14	**5**	0.5	3	**13**	15[e]	B[f]	20[f]	**19**	60[f]
15	**6a**	5	17	**14a**	73	B	15	**20a**	95
16	**6b**	4	8	**14b**	49	B	8	**20b**	70
17	**7a**	4	1	**15a**	76	B	2	**21a**	95
18	**7b**	4.5	1	**15b**	71	B	2	**21b**	94
19	**8**[g]	1	2	**16**	65				

[a] Time necessary for the oxidation to the selenoxides. [b] Time necessary for the elimination reactions. [c] Based on isolated products after column chromatography. In the case of the elimination products reaction yields were calculated from the amount of the selenide employed. [d] A: Amberlist, B: DBU. [e] Most of the product is converted into the aromatic derivative **19** during column chromatography. [f] In this experiment the selenoxides were directly allowed to react with DBU in refluxing benzene. [g] This reaction was carried out on the trans isomer.

Chart III



Scheme III



ature[14] for the synthesis of these classes of compounds, which are largely distributed in nature and have a wide range of practical applications.[14]

Finally, the elimination of the selenoxide deriving from the γ-lactone **8** gave the γ-methylene γ-lactone **16** in good yield. γ-Methylene γ-lactones present an interesting chemical behavior since they can react with both electrophilic and nucleophilic reagents.[15] Moreover, they also have important biological activities.[16] The selenoxide elimination reaction represents a convenient synthesis of these compounds since seleno lactones, having structures similar to **8**, are readily available.[6,7]

In conclusion the elimination reactions of the terminal β-oxy selenoxides having the general structure indicated in Scheme II, as well as those of their sulfur analogs, seem to be of general validity and very likely can find other useful applications in organic synthesis.

Experimental Section

Products identifidation was effected by proton and carbon-13 NMR spectroscopy, mass spectrometry, and elemental analyses.[17]

Preparation of the Starting Selenides. Compounds **3b**, **3d**, **3f**, **4a**, **5**, **6a**,[7] **7a**,[18] and **8**[6] have already been described in the literature. Compounds **1a** and **1b** were obtained from the phenylselenenylation[5] of 1-octene, in nitromethane,[19] in the presence of an excess of *p*-methylphenol and *p*-nitrophenol, respectively. Reaction yields are reported in parentheses.

1-(Phenylseleno)-2-(*p*-methylphenoxy)octane (1a): oil (65%); ^{1}H NMR δ 7.55–7.45 (m, 2 H), 7.3–7.2 (m, 3 H), 7.0 and 6.52 (AA'BB', 4 H), 4.38–4.22 (m, 1 H), 3.21 (dd, 1 H, *J* = 4.8 and 12.4 Hz), 3.02 (dd, 1 H, *J* = 7.2 and 12.4 Hz), 2.25 (s, 3 H), 2.0–1.6 (m, 2 H), 1.5–1.2 (m, 8 H), 0.9 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR δ 163.1, 141.2, 133.3, 129.9, 129.0, 127.1, 116.1, 77.8, 34.0, 31.9, 31.7, 29.2, 25.3, 22.5, 20.4, 14.0; MS *m/z* (relative intensity) 376 (1), 271 (9), 270 (8), 269 (53), 267 (27), 266 (10), 265 (11), 171 (14), 157 (14), 108 (12), 107 (14), 91 (16), 77 (15), 69 (100), 55 (38). Anal. Calcd for $C_{21}H_{28}N_3Se$: C, 67.19; H, 7.52. Found: C, 67.27; H, 7.60.

1-(Phenylseleno)-2-(*p*-nitrophenoxy)octane (1b): oil (37%); ^{1}H NMR δ 8.15–8.05 (m, 2 H), 7.6–7.5 (m, 2 H), 7.37–7.2 (m, 3 H), 6.75–6.6 (m, 2 H), 4.52–4.38 (m, 1 H), 3.15 (dd, 1 H, *J* = 5.2 and 12.8 Hz), 3.03 (dd, 1 H, *J* = 6.9 and 12.8 Hz), 2.0–1.65 (m, 2 H), 1.5–1.1 (m, 8 H), 0.89 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR δ 163.1, 141.3, 133.7, 129.1, 127.6, 125.7, 115.1, 78.3, 33.7, 31.5, 31.3, 28.9, 25.1, 22.4, 13.9; MS *m/z* (relative intensity) 407 (8), 269 (57), 171 (13), 157 (22), 91 (15), 69 (100), 55 (58), 43 (18), 41 (42). Anal. Calcd for $C_{20}H_{25}NO_3Se$: C, 59.11; H, 6.20; N, 3.45. Found: C, 59.19; H, 6.14; N, 3.52.

Compounds **2a** and **2b** were prepared by 1-phenyl-2-(phenylselenenyl)ethanol and 1-(phenylselenenyl)-2-octanol,[5] respectively. Excess sodium hydride was added to a solution of the alcohol in THF. The resulting mixture, cooled at −20 °C, was treated with methyl propiolate, and the progress of the reaction was monitored by TLC and MS. After the usual workup the products were purified by column chromatography. Reaction yields are reported in parentheses.

Methyl 5-phenyl-6-(phenylseleno)-4-oxa-2-hexenoate (2a): oil (58%); ^{1}H NMR δ 7.55–7.45 (m, 2 H), 7.46 (d, 1 H, *J* = 12.5 Hz), 7.4–7.2 (m, 8 H), 5.18 (d, 1 H, *J* = 12.5 Hz), 4.99 (dd, 1 H, *J* = 5.3 and 8.1 Hz), 3.63 (s, 3 H), 3.38 (dd, 1 H, *J* = 8.1 and

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13.0 Hz), 3.18 (dd, 1 H, J = 5.3 and 13.0 Hz); ^{13}C NMR δ 167.8, 161.1, 138.9, 133.3, 129.2, 128.8, 127.8, 125.8, 98.6, 83.8, 72.3, 50.9, 38.4, 34.3; MS m/z (relative intensity) 261 (33), 183 (100), 157 (50), 104 (72), 77 (42). Anal. Calcd for $C_{18}H_{18}O_3Se$: C, 59.84; H, 5.02. Found: C, 59.92; H, 5.08.

Methyl 5-[(phenylseleno)methyl]-4-oxa-2-undecenoate (2b): oil (50%); ^{1}H NMR δ 7.6–7.48 (m, 2 H), 7.45 (d, 1 H, J = 12.3 Hz), 7.31–7.2 (m, 3 H), 5.16 (d, 1 H, J = 12.3 Hz), 4.1–3.9 (m, 1 H), 3.69 (s, 3 H), 3.1–3.0 (m, 2 H), 1.82–1.58 (m, 2 H), 1.4–1.1 (m, 8 H), 0.89 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ 168.2, 162.1, 133.3, 129.2, 127.4, 97.1, 83.3, 50.8, 34.2, 31.8, 31.5, 28.9, 25.0, 22.4, 13.9; MS m/z (relative intensity) 370 (6), 269 (47), 171 (13), 157 (21), 91 (16), 85 (49), 77 (13), 69 (100), 55 (52), 43 (18), 41 (37). Anal. Calcd for $C_{18}H_{26}O_3Se$: C, 58.54; H, 7.10. Found: C, 58.61; H, 7.04.

Compounds **3a**, **3c**, **3e**, **3g**, **4b**, **6b**, and **7b** were obtained by selenium-induced ring-closure reactions, according to our recently described procedure.[7] Reaction yields are reported in parentheses. An easily separable mixture of **3c** and **3g** was obtained from the reaction of allyl benzoylacetone. The allyl derivatives necessary for these reactions were prepared by standard methods.

3-Carbethoxy-4,5-dihydro-2-phenyl-5-[(phenylseleno)methyl]furan (3a): oil (77%); ^{1}H NMR δ 7.75–7.60 (m, 2 H), 7.60–7.45 (m, 2 H), 7.4–7.1 (m, 6 H), 4.86 (ddt, 1 H, J = 5.5, 7.3, and 10.0 Hz), 4.1 (q, 2 H, J = 7.1 Hz), 3.3 (dd, 1 H, J = 5.5 and 12.5 Hz), 3.25 (dd, 1 H, J = 10.0 and 15.4 Hz), 3.08 (dd, 1 H, J = 7.3 and 12.5 Hz), 2.9 (dd, 1 H, J = 7.3 and 15.4 Hz), 1.18 (t, 3 H, J = 7.1 Hz); ^{13}C NMR δ 165.0, 164.3, 133.2, 130.2, 129.2, 127.4, 127.2, 102.0, 80.3, 59.6, 37.2, 32.5, 14.2; MS m/z (relative intensity) 388 (11), 231 (24), 185 (40), 157 (13), 105 (100), 77 (39). Anal. Calcd for $C_{20}H_{20}O_3Se$: C, 62.02; H, 5.20. Found: C, 62.07; H, 5.13.

3-Acetyl-4,5-dihydro-2-phenyl-5-[(phenylseleno)methyl]furan (3c): oil (37%); ^{1}H NMR δ 7.6–7.1 (m, 10 H), 4.9 (ddt, 1 H, J = 5.6, 7.2, and 10.6 Hz), 3.28 (dd, 1 H, J = 5.6 and 12.4 Hz), 3.25 (dd, 1, H, J = 10.6 and 15.4 Hz), 3.1 (dd, 1 H, J = 7.2 and 12.4 Hz), 2.94 (dd, 1 H, J = 7.4 and 15.4 Hz), 1.95 (s, 3 H); ^{13}C NMR δ 193.9, 165.1, 133.0, 130.3, 129.0, 128.0, 127.2, 114.0, 80.9, 37.0, 32.5, 28.7; MS m/z (relative intensity) 358 (8), 201 (51), 199 (12), 183 (10), 157 (10), 105 (88), 91 (13), 77 (44), 51 (12), 43 (100). Anal. Calcd for $C_{19}H_{18}O_2Se$: C, 63.87; H, 5.08. Found: C, 63.81; H, 5.00.

4,5-Dihydro-2-phenyl-5-[(phenylseleno)methyl]-3-(phenylsulfonyl)furan (3e): oil (67%); ^{1}H NMR δ 7.75–7.65 (m, 2 H), 7.6–7.5 (m, 2 H), 7.5–7.25 (m, 7 H), 7.2–7.1 (m, 4 H), 4.95–4.75 (m, 1 H), 3.25 (dd, 1 H, J = 10.2 and 14.7 Hz), 3.15 (dd, 1 H, J = 5.2 and 12.8 Hz), 3.01 (dd, 1 H, J = 7.0 and 12.8 Hz), 2.93 (dd, 1 H, J = 7.2 and 14.7 Hz); ^{13}C NMR δ 163.1, 141.6, 132.8, 132.5, 130.6, 129.2, 129.0, 128.6, 128.0, 127.4, 127.2, 126.6, 109.8, 80.3, 37.3, 32.0. Anal. Calcd for $C_{23}H_{20}O_3SeS$: C, 60.66; H, 4.43. Found: C, 60.58; H, 4.38.

3-Benzoyl-4,5-dihydro-2-methyl-5-[(phenylseleno)methyl]furan (3g): oil (57%); ^{1}H NMR δ 7.7–7.2 (m, 10 H), 4.84 (ddt, 1 H, J = 5.6, 7.0, and 9.9 Hz), 3.25 (dd, 1 H, J = 5.6 and 12.6 Hz), 3.1 (dd, 1 H, J = 7.0 and 12.6 Hz), 3.3–3.1 (m, 1 H), 2.9 (ddq, 1 H, J = 1.4, 7.3, and 14.7 Hz), 1.77 (t, 3 H, J = 1.4 Hz); ^{13}C NMR δ 192.7, 168.2, 142.0, 133.2, 130.9, 129.1, 128.4, 128.1, 127.6, 127.3, 126.4, 124.9, 112.0, 81.2, 36.9, 32.6, 15.2; MS m/z (relative intensity) 358 (5), 201 (53), 183 (10), 157 (11), 105 (100), 91 (12), 77 (50), 43 (56). Anal. Calcd for $C_{19}H_{18}O_2Se$: C, 63.87; H, 5.08. Found: C, 63.94; H, 5.01.

2-[[5-(Phenylseleno)methyl]tetrahydrofuryliden]-acetophenone (4b): oil (58%); ^{1}H NMR δ 7.9–7.8 (m, 2 H), 7.6–7.5 (m, 2 H), 7.5–7.3 (m, 3 H), 7.3–7.2 (m, 3 H), 6.48 (t, 1 H, J = 1.5 Hz), 4.68 (ddt, 1 H, J = 5.5, 7.0, and 7.2 Hz), 3.48 (dddd, 1 H, J = 1.5, 4.6, 9.3, and 19.0 Hz), 3.28–3.12 (m, 1 H), 3.22 (dd, 1 H, J = 5.5 and 12.6 Hz), 3.04 (dd, 1 H, J = 7.2 and 12.6 Hz), 2.31 (dddd, 1 H, J = 4.6, 6.7, 11.5, and 17.3 Hz), 1.88 (ddt, 1 H, J = 8.3, 9.3, and 12.8 Hz); ^{13}C NMR δ 195.9, 178.1, 139.7, 133.1, 131.6, 129.2, 128.3, 127.5, 95.2, 83.1, 31.5, 29.1; MS m/z (relative intensity) 358 (6), 201 (30), 157 (11), 147 (48), 105 (100), 77 (34), 69 (21), 55 (12), 51 (10). Anal. Calcd for $C_{19}H_{18}O_2Se$: C, 63.87; H, 5.08. Found: C, 63.93; H, 5.01.

5-[(Phenylseleno)methyl]-2-(2-thienyl)-4,5-dihydrooxazole (6b): oil (67%); ^{1}H NMR δ 7.6–7.5 (m, 2 H), 7.49 (d, 1 H, J = 3.6 Hz), 7.4 (d, 1 H, J = 5.0 Hz), 7.3–7.2 (m, 3 H), 7.02 (t, 1 H, J = 4.9 Hz), 4.94–4.78 (m, 1 H), 4.12 (dd, 1 H, J = 9.2 and 14.9 Hz), 3.8 (dd, 1 H, J = 6.8 and 14.9 Hz), 3.25 (dd, 1 H, J = 5.2 and 12.7 Hz), 3.02 (dd, 1 H, J = 7.7 and 12.7 Hz); ^{13}C NMR δ 159.2, 133.1, 130.0, 129.6, 129.0, 128.6, 127.3, 79.2, 60.0, 31.5; MS m/z (relative intensity) 323 (10), 165 (33), 152 (13), 136 (28), 111 (100), 110 (20), 97 (13). Anal. Calcd for $C_{14}H_{13}NOSeS$: C, 52.18; H, 4.07; N, 4.35. Found: C, 52.25; H, 4.14; N, 4.43.

5-[(Phenylseleno)methyl]-2-(2-thienyl)-4,5-dihydrothiazole (7b): mp 92–93 °C (70%); ^{1}H NMR δ 7.58–7.47 (m, 2 H), 7.42 (d, 1 H, J = 5.0 Hz), 7.38 (d, 1 H, J = 3.7 Hz), 7.32–7.18 (m, 3 H), 7.03 (dd, 1 H, J = 3.7 and 5.0 Hz), 4.5 (dd, 1 H, J = 3.1 and 16.0 Hz), 4.22 (dd, 1 H, J = 7.7 and 16.0 Hz), 4.12–3.98 (m, 1 H), 3.12 (dd, 1 H, J = 6.4 and 12.6 Hz), 3.02 (dd, 1 H, J = 8.9 and 12.6 Hz); ^{13}C NMR δ 160.2, 137.1, 133.5, 130.7, 129.7, 129.2, 128.8, 127.6, 127.4, 68.9, 51.8, 33.4. Anal. Calcd for $C_{14}H_{13}NSeS_2$: C, 49.70; H, 3.87; N, 4.14. Found: C, 49.76; H, 3.92; N, 4.20.

Preparation of Selenoxides and Elimination Reactions. General Procedure. Excess hydrogen peroxide (4–6 mmol) was added to a solution of the selenide (2–3 mmol) in methanol (30–40 mL), and the mixture was stirred at room temperature for the time indicated in Table I. The progress of the oxidation could be easily followed by TLC. The solvent was evaporated under reduced pressure, and the residue was dissolved in methylene chloride and washed with water. The organic phase was dried and evaporated. Proton NMR analysis of the residue showed the presence of two diastereoisomeric selenoxides in comparable amounts. The crude selenoxides were dissolved in benzene (30 mL), and 10% sodium bicarbonate (10 mL) was added. The mixture was refluxed under vigorous stirring for the time indicated in Table I. The progress of the reaction was followed by TLC. After cooling the reaction was worked up in the usual way and the residue was chromatographed on a silica gel column using mixtures of light petroleum end ethyl ether as eluants. Reaction yields are reported in Table I. Compound **16** has already been described in the literature.[20] Physical and spectral data of the other reaction products are reported below.

2-(*p*-Methylphenoxy)-1-octene (9a): oil; ^{1}H NMR δ 7.15 and 6.92 (AA'BB', 4 H), 4.08 (d, 1 H, J = 1.6 Hz), 3.88 (d, 1 H, J = 1.6 Hz), 2.32 (s, 3 H), 2.23 (t, 2 H, J = 7.0 Hz), 1.61 (quint, 2 H, J = 7.1 Hz), 1.5–1.2 (m, 6 H), 0.92 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ 164.0, 153.3, 133.2, 130.0, 120.7, 87.8, 34.1, 31.7, 28.8, 27.1, 22.6, 20.7, 14.0; MS m/z (relative intensity) 218 (1), 148 (15), 110 (11), 108 (100), 107 (20), 105 (16), 81 (10), 43 (11). Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.58; H, 10.23.

2-(*p*-Nitrophenoxy)-1-octene (9b): oil; ^{1}H NMR δ 8.2 and 7.1 (AA'BB', 4 H), 4.55–4.5 (m, 1 H), 4.38–4.35 (m, 1 H), 2.27 (t, 2 H, J = 7.0 Hz), 1.7–1.5 (m, 2 H), 1.48–1.12 (m, 6 H), 0.92 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ 161.6, 161.2, 143.0, 125.7, 118.7, 95.1, 33.3, 31.5, 28.6, 26.7, 22.5, 13.9; MS m/z (relative intensity) 179 (33), 139 (35), 137 (25), 131 (20), 111 (47), 110 (34), 109 (23), 81 (20), 69 (100), 55 (56), 43 (82), 41 (74). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.52; H, 7.61; N, 5.54.

Methyl 5-phenyl-4-oxa-2,5-hexadienoate (10a): oil; ^{1}H NMR δ 7.75 (d, 1 H, J = 12.2 Hz), 7.6–7.5 (m, 2 H), 7.4–7.3 (m, 3 H), 5.67 (d, 1 H, J = 12.2 Hz), 5.14 (d, 1 H, J = 3.2 Hz), 4.75 (d, 1 H, J = 3.2 Hz), 3.71 (s, 3 H); ^{13}C NMR δ 167.4, 158.6, 158.1, 133.5, 129.3, 128.5, 125.3, 102.4, 93.3, 51.2; MS m/z (relative intensity) 204 (3), 173 (2), 145 (6), 105 (51), 103 (100), 77 (31), 51 (8). Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.64; H, 5.98.

Methyl 5-(1-hexyl)-4-oxa-2,5-hexadienoate (10b): oil; ^{1}H NMR δ 7.65 (d, 1 H, J = 12.2 Hz), 5.53 (d, 1 H, J = 12.2 Hz), 4.38 (d, 1 H, J = 2.7 Hz), 4.33 (dt, 1 H, J = 0.7 and 2.7 Hz), 3.73 (s, 3 H), 2.18 (t, 2 H, J = 7.0 Hz), 1.59–1.41 (m, 2 H), 1.4–1.23 (m, 6 H), 0.9 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ 167.7, 162.0, 157.5, 101.8, 91.2, 51.1, 33.5, 31.5, 28.6, 26.6, 22.5, 14.0; MS m/z (relative intensity) 181 (5), 142 (5), 111 (45), 110 (15), 100 (27), 85 (10), 83 (19), 72 (17), 71 (45), 69 (100), 55 (54), 43 (64), 41 (61). Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.90; H, 9.50. Found: C, 67.97; H, 9.42.

3-Carbethoxy-4,5-dihydro-2-phenyl-5-methylenefuran (11a): oil; ^{1}H NMR δ 8.1–7.8 (m, 2 H), 7.5–7.2 (m, 3 H), 4.72 (q, 1 H, J = 2.9 Hz), 4.33 (q, 2 H, J = 2.9 Hz), 4.15 (q, 2 H, J = 7.0 Hz), 3.82 (t, 2 H, J = 2.9 Hz), 1.2 (t, 3 H, J = 7.0 Hz); ^{13}C NMR

(20) Krafft, G. A.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 5459.

(C_6D_6) δ 164.5, 159.4, 133.2, 130.5, 130.2, 129.7, 129.6, 129.3, 85.6, 59.6, 35.7, 14.1; MS *m/z* (relative intensity) 230 (98), 202 (46), 201 (34), 185 (100), 157 (41), 128 (25), 115 (14), 105 (55), 77 (42), 51 (12), 43 (24). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.93; H, 6.05.

3-Benzoyl-4,5-dihydro-2-phenyl-5-methylenefuran (11b): oil, ^{1}H NMR δ 7.6–7.4 (m, 2 H), 7.4–6.8 (m, 8 H), 4.8 (q, 1 H, *J* = 2.8 Hz), 4.35 (q, 1 H, *J* = 2.8 Hz), 3.9 (t, 2 H, *J* = 2.8 Hz); ^{13}C NMR (C_6D_6) δ 191.6, 161.4, 160.0, 138.9, 131.6, 130.1, 129.3, 128.5, 128.0, 127.9, 127.5, 113.2, 86.1, 37.1; MS *m/z* (relative intensity) 262 (38), 261 (11), 185 (12), 157 (31), 105 (100), 77 (79), 51 (15). Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.43; H, 5.38. Found: C, 82.35; H, 5.31.

3-Acetyl-4,5-dihydro-5-methylene-2-phenylfuran (11c): oil; ^{1}H NMR δ 7.7–7.55 (m, 2 H), 7.55–7.35 (m, 3 H), 4.7 (q, 1 H, *J* = 2.8 Hz), 4.35 (q, 1 H, *J* = 2.8 Hz), 3.8 (t, 2 H, *J* = 2.8 Hz), 2.0 (s, 3 H); ^{13}C NMR δ 193.1, 163.4, 159.2, 130.8, 129.7, 129.2, 128.3, 115.5, 86.3, 35.0, 28.8; MS *m/z* (relative intensity) 200 (100), 185 (88), 157 (72), 129 (20), 128 (26), 115 (19), 105 (76), 77 (55), 51 (21), 43 (95). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.04; H, 6.11.

3-Cyano-4,5-dihydro-5-methylene-2-phenylfuran (11d): oil; ^{1}H NMR δ 8.0–7.8 (m, 2 H), 7.5–7.2 (m, 3 H), 4.75 (q, 1 H, *J* = 2.7 Hz), 4.28 (q, 1 H, *J* = 2.7 Hz), 3.6 (t, 2 H, *J* = 2.7 Hz); ^{13}C NMR δ 157.6, 151.6, 131.1, 128.6, 126.6, 114.8, 95.0, 87.4, 35.1; MS *m/z* (relative intensity) 183 (100), 182 (43), 154 (20), 140 (14), 127 (12), 105 (96), 77 (76), 51 (30). Anal. Calcd for $C_{12}H_9NO$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.73; H, 5.02; N, 7.75.

4,5-Dihydro-5-methylene-2-phenyl-3-(phenylsulfonyl)furan (11e): oil; ^{1}H NMR δ 7.85–7.6 (m, 4 H), 7.6–7.3 (m, 6 H), 4.73 (q, 1 H, *J* = 2.9 Hz), 4.45 (q, 1 H, *J* = 2.9 Hz), 3.83 (t, 2 H, *J* = 2.9 Hz); ^{13}C NMR δ 161.6, 157.2, 141.3, 133.0, 131.2, 129.4, 128.9, 127.8, 127.3, 127.0, 112.3, 87.4, 35.9. Anal. Calcd for $C_{17}H_{14}O_3S$: C, 68.44; H, 4.73. Found: C, 68.51; H, 4.78.

3-Carbomethoxy-4,5-dihydro-2-methyl-5-methylenefuran (11f): oil; ^{1}H NMR δ 4.6 (q, 1 H, *J* = 2.9 Hz), 4.25 (q, 1 H, *J* = 2.6 Hz), 3.72 (s, 3 H), 3.55 (dt, 2 H, *J* = 2.0 and 4.6 Hz), 2.25 (t, 3 H, *J* = 1.9 Hz); ^{13}C NMR (C_6D_6) δ 165.8, 160.4, 133.5, 129.3, 85.8, 50.5, 33.7, 13.3; MS *m/z* (relative intensity) 154 (47), 139 (37), 123 (33), 95 (100), 81 (12), 59 (10), 43 (74). Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.26; H, 6.47.

3-Benzoyl-4,5-dihydro-2-methyl-5-methylenefuran (11g): oil; ^{1}H NMR δ 7.7–7.3 (m, 5 H), 4.65 (q, 1 H, *J* = 2.8 Hz), 4.35 (q, 1 H, *J* = 2.8 Hz), 3.9–3.65 (m, 2 H), 1.9 (t, 3 H, *J* = 2.0 Hz); ^{13}C NMR δ 186.5, 165.8, 159.6, 131.4, 128.8, 128.3, 127.8, 113.7, 86.0, 34.6, 14.8; MS *m/z* (relative intensity) 200 (100), 199 (88), 185 (10), 171 (11), 157 (26), 129 (12), 123 (99), 105 (77), 77 (92), 53 (16), 51 (36), 43 (84). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.92; H, 6.09.

Methyl [2-(5-methylene)tetrahydrofuryliden]acetate (12a): oil; ^{1}H NMR (C_6D_6) δ 5.6 (t, 1 H, *J* = 1.9 Hz), 4.52 (q, 1 H, *J* = 1.9 Hz), 3.92 (q, 1 H, *J* = 1.9 Hz), 3.3 (s, 3 H), 2.9 (dt, 2 H, *J* = 1.9 and 8.3 Hz), 2.08 (tt, 2 H, *J* = 1.9 and 8.5 Hz); ^{13}C NMR δ 174.0, 167.8, 160.7, 92.0, 85.2, 50.4, 28.8, 25.7; MS *m/z* (relative intensity) 154 (53), 123 (92), 122 (13), 95 (33), 94 (16), 69 (100), 66 (11), 55 (12), 53 (11), 43 (32), 42 (10), 41 (10). Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.70; H, 6.61.

[2-(5-Methylene)tetrahydrofuryliden]acetophenone (12b): mp 65–68 °C; ^{1}H NMR δ 7.98–7.85 (m, 2 H), 7.57–7.4 (m, 3 H), 6.67 (t, 1 H, *J* = 1.8 Hz), 4.68 (q, 1 H, *J* = 2.1 Hz), 4.28 (q, 1 H, *J* = 2.0 Hz), 3.36 (dt, 2 H, *J* = 1.8 and 8.0 Hz), 2.78 (tt, 2 H, *J* = 1.8 and 8.8 Hz); ^{13}C NMR δ 190.3, 175.8, 160.1, 139.3, 132.0, 128.4, 127.6, 96.7, 86.1, 29.8, 25.7; MS *m/z* (relative intensity) 200 (55), 199 (11), 123 (47), 105 (100), 95 (28), 77 (55), 69 (40), 51 (16), 43 (11). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.04; H, 5.99.

2,3-Dihydro-2-methylenebenzofuran (13): oil; ^{1}H NMR δ 7.3–6.7 (m, 4 H), 4.7 (q, 1 H, *J* = 2.7 Hz), 4.3 (q, 1 H, *J* = 2.7 Hz), 3.9 (br s, 2 H).

2-Phenyl-5-methylene-4,5-dihydrooxazole (14a): oil; ^{1}H NMR δ 8.1–7.9 (m, 2 H), 7.3–7.1 (m, 3 H), 4.7 (q, 1 H, *J* = 2.7 Hz), 4.37 (t, 2 H, *J* = 2.7 Hz), 4.1 (q, 1 H, *J* = 2.7 Hz); ^{13}C NMR δ 163.3, 159.7, 131.6, 128.6, 128.4, 127.6, 83.4, 59.0; MS *m/z* (relative intensity) 159 (30), 131 (28), 117 (100), 91 (12), 90 (11), 89 (12), 77 (37), 51 (19). Anal. Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.51; H, 5.77; N, 8.87.

5-Methylene-2-(2-thienyl)-4,5-dihydrooxazole (14b): oil; ^{1}H NMR δ 7.65 (d, 1 H, *J* = 3.7 Hz), 7.49 (d, 1 H, *J* = 4.8 Hz), 7.1 (dd, 1 H, *J* = 3.7 and 4.8 Hz), 4.8 (q, 1 H, *J* = 2.9 Hz), 4.62 (t, 2 H, *J* = 2.8 Hz), 4.35 (q, 1 H, *J* = 2.8 Hz); ^{13}C NMR δ 159.3, 158.4, 139.0, 130.6, 130.2, 127.5, 83.8, 57.4; MS *m/z* (relative intensity) 165 (70), 137 (39), 123 (100), 122 (19), 111 (14), 109 (18), 97 (14), 96 (41), 70 (11), 69 (10), 45 (12). Anal. Calcd for C_8H_7NOS: C, 58.16; H, 4.27; N, 8.48. Found: C, 58.23; H, 4.35; N, 8.58.

5-Methylene-2-phenyl-4,5-dihydrothiazole (15a): oil; ^{1}H NMR δ 7.85–7.7 (m, 2 H), 7.5–7.35 (m, 3 H), 5.32–5.24 (m, 2 H), 5.16 (t, 2 H, *J* = 2.8 Hz); ^{13}C NMR δ 147.9, 141.4, 131.3, 128.5, 128.0, 103.2, 71.7; MS *m/z* (relative intensity) 177 (3), 176 (7), 175 (57), 72 (100), 71 (43), 45 (9). Anal. Calcd for $C_{10}H_9NS$: C, 68.54; H, 5.18; N, 7.99. Found: C, 68.62; H, 5.08; N, 7.92.

5-Methylene-2-(2-thienyl)-4,5-dihydrothiazole (15b): oil; ^{1}H NMR δ 7.42 (d, 1 H, *J* = 5.0 Hz), 7.32 (d, 1 H, *J* = 3.7 Hz), 7.03 (dd, 1 H, *J* = 3.7 and 5.0 Hz), 5.25 (dt, 1 H, *J* = 2.5 and 1.7 Hz), 5.21 (dt, 1 H, *J* = 1.7 and 3.0 Hz), 3.07 (t, 2 H, *J* = 2.8 Hz); ^{13}C NMR δ 159.5, 147.6, 136.6, 130.2, 129.5, 127.2, 103.3, 70.9. Anal. Calcd for $C_8H_7NS_2$: C, 53.03; H, 3.87; N, 7.73. Found: C, 52.98; H, 3.81; N, 7.67.

Aromatization Reactions. General Procedure. Amberlist or DBU (0.2–0.4 mmol) was added to a solution of the elimination products (1–2 mmol) in benzene (30 mL) and the mixture was stirred at room temperature or at 50 °C, respectively, for the time indicated in Table I. The progress of the reaction was followed by TLC. After evaporation of the solvent the residue was chromatographed through a silica gel column. The method employed and the reaction yields are reported in Table I. The 2-methylbenzofuran, **19**, is a commercial product. Compounds **17c**,[21] **17f**,[22] **17g**,[23] **18b**,[23] **20a**[24] and **21a**[25] have already been described in the literature. Physical and spectral data of the other reaction products are reported below.

3-Carbethoxy-5-methyl-2-phenylfuran (17a): oil;[11] ^{1}H NMR δ 8.05–7.09 (m, 2 H), 7.5–7.2 (m, 3 H), 6.45 (s, 1 H), 4.1 (q, 2 H, *J* = 7.0 Hz), 2.35 (s, 3 H), 1.1 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR δ 128.8, 128.2, 128.0, 127.7, 108.8, 60.3, 14.2, 13.2; MS *m/z* (relative intensity) 231 (14), 230 (93), 202 (50), 201 (16), 186 (14), 185 (100), 128 (17), 115 (10), 105 (37), 77 (30), 51 (11), 43 (34).

3-Benzoyl-5-methyl-2-phenylfuran (17b): oil;[11] ^{1}H NMR δ 7.9–7.75 (m, 2 H), 7.75–7.6 (m, 2 H), 7.6–7.15 (m, 6 H), 6.25 (s, 1 H), 2.35 (s, 3 H); ^{13}C NMR δ 191.6, 154.3, 150.9, 132.4, 129.5, 128.4, 127.1, 126.1, 109.7, 13.2; MS *m/z* (relative intensity) 262 (100), 261 (62), 185 (57), 105 (92), 77 (76), 51 (13).

3-Cyano-5-methyl-2-phenylfuran (17d): oil; ^{1}H NMR δ 7.95–7.8 (m, 2 H), 7.2–6.95 (m, 3 H), 5.65 (s, 1 H), 1.8 (s, 3 H); ^{13}C NMR δ 158.1, 152.3, 129.5, 129.0, 125.1, 112.0, 109.1, 92.7, 12.7; MS *m/z* (relative intensity) 183 (100), 182 (39), 140 (20), 105 (55), 77 (37), 51 (16). Anal. Calcd for $C_{12}H_9NO$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.62; H, 4.90; N, 7.58.

5-Methyl-2-phenyl-3-(phenylsulfonyl)furan (17e): mp 120–122 °C (lit.[12] mp 106–107 °C); ^{1}H NMR δ 7.94–7.75 (m, 4 H), 7.5–7.25 (m, 6 H), 6.45 (q, 1 H, *J* = 1.0 Hz), 2.3 (d, 3 H, *J* = 1.0 Hz); ^{13}C NMR δ 151.7, 142.2, 133.0, 129.6, 129.3, 128.9, 128.5, 128.3, 128.2, 126.9, 108.4, 13.3; MS *m/z* (relative intensity) 300 (6), 299 (19), 298 (100), 129 (26), 128 (23), 105 (11), 77 (24), 51 (17), 43 (30).

2-[(Carbomethoxy)methyl]-5-methylfuran (18a): oil; ^{1}H NMR δ 6.1 (d, 1 H, *J* = 2.9 Hz), 5.9 (d, 1 H, *J* = 2.9 Hz), 3.72 (s, 3 H), 3.63 (br s, 2 H), 2.27 (br s, 3 H); ^{13}C NMR δ 169.9, 151.6, 145.7, 108.7, 106.3, 52.0, 33.9, 13.4; MS *m/z* (relative intensity) 154 (16), 95 (100), 43 (11). Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.26; H. 6.47.

5-Methyl-2-(2-thienyl)oxazole (20b): oil; ^{1}H NMR δ 7.6 (dd, 1 H, *J* = 1.2 and 3.7 Hz), 7.38 (dd, 1 H, *J* = 1.2 and 5.1 Hz), 7.09 (dd, 1 H, *J* = 3.7 and 5.1 Hz), 6.78 (q, 1 H, *J* = 1.2 Hz), 2.38 (d, 3 H, *J* = 1.2 Hz); ^{13}C NMR δ 156.7, 148.3, 130.4, 127.6, 127.4, 126.7, 123.9, 10.8; MS *m/z* (relative intensity) 165 (91), 137 (41),

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123 (100), 122 (31), 111 (18), 109 (19), 96 (44), 65 (15), 45 (16). Anal. Calcd for C_8H_7NOS: C, 58.16; H, 4.27; N, 8.48. Found: C, 58.07; H, 4.20; N, 8.39.

5-Methyl-2-(2-thienyl)thiazole (21b): oil; ^1H NMR δ 7.38 (dd, 1 H, J = 1.0 and 4.0 Hz), 7.37 (br s, 1 H), 7.31 (dd, 1 H, J = 1.0 and 5.0 Hz), 7.01 (dd, 1 H, J = 4.0 and 5.0 Hz), 2.44 (d, 3 H, J = 1.0 Hz); ^{13}C NMR δ 160.2, 140.7, 137.6, 133.1, 127.6, 126.8, 125.7, 11.8; MS m/z (relative intensity) 181 (78), 72 (100), 71 (49), 45 (17). Anal. Calcd for $C_8H_7NS_2$: C, 53.01; H, 3.89; N, 7.73. Found: C, 53.08; H, 3.96; N, 7.80.

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