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PHENYLSELENO-LACTONIZATION OF OLEFINIC NITRILES PROMOTED BY PEROXYDISULPHATE ION OXIDATION OF DIPHENYL DISELENIDE

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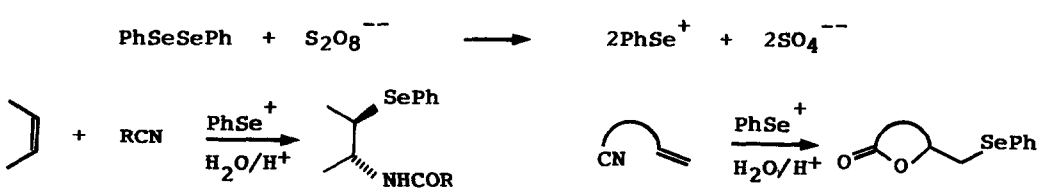
The oxidation of diphenyl diselenide with ammonium peroxydisulphate is a very simple and efficient method to produce phenylselenium cations in the absence of nucleophilic counter ions. The reaction carried out in the presence of an olefin, in acetonitrile or propionitrile containing trifluoromethanesulphonic acid and water afforded the amidoselenenylation products in good yield. The intramolecular version of this reaction, using appropriate unsaturated nitriles as the starting products and dioxane as solvent, took a different course and afforded phenylselenolactones in good yield. This new selenium induced ring closure reaction proceeded through the initial formation of the hydroxyselenenylation products in which the hydrolysis of the cyano group is suggested to be intramolecularly assisted by the hydroxy group.

The addition of phenylselenium cations to unsaturated compounds has been largely used as a crucial step of many important synthetic transformations.[1,2] We have recently reported that the oxidation of diphenyl diselenide with ammonium peroxydisulphate can be conveniently employed to produce phenylselenium cations in the absence of nucleophilic counter ions.[3,4] This aspect has a considerable synthetic relevance and our simple procedure presents several advantages over other previously described methods. The most common source of phenylselenium cations is the commercially available phenylselenenyl chloride; however, the presence of the chloride ion is often responsible for some undesirable processes such as

incorporation of chlorine and decrease in selectivity. Furthermore, the addition of PhSeCl to an alkene is sometimes complicated by the fact that the formed phenyl alkyl selenides further react with PhSeCl to afford the deselenenylated products.[5,6] Several phenylselenenylating agents which have a non-nucleophilic counter ion have been introduced in the literature. N-Phenylselenophtalimide,[7] $PhSeSbF_6$,[8] $PhSePF_6$,[8] and $PhSeOSO_2CF_3$[9,10] have been employed as useful substituted of PhSeCl. In a much simpler way we have found that the reaction of PhSeSePh with $(NH_4)_2S_2O_8$ can be used to effect the alkoxyselenenylation and the hydroxyselenenylation of alkenes.[3] Moreover, several kinds of selenium induced ring closure reactions were also successfully carried out starting from alkenes containing internal nucleophiles.[4] Thus unsaturated alcohols, amides, β-diketones and β-ketoesters gave the products of seleno-etherification. The same process occurred with dienes and with unsaturated ketones when the reactions were effected in the presence of water or methanol, respectively. Unsaturated acids, esters and imides afforded the phenylseleno-lactonization products.

We now report that, using nitriles as solvents, in the presence of trifluoromethanesulphonic acid and water, the oxidation of diphenyl diselenide with ammonium peroxydisulphate can also be used to effect the amidoselenenylation of alkenes. We also report that the intramolecular version of this reaction, using unsaturated nitriles as the starting products and dioxane as solvent, takes a different course and affords the products of seleno-lactonization in good yield (Scheme 1). This simple reaction represents a new and convenient method to synthesize this kind of compounds and it has been investigated in some detail.

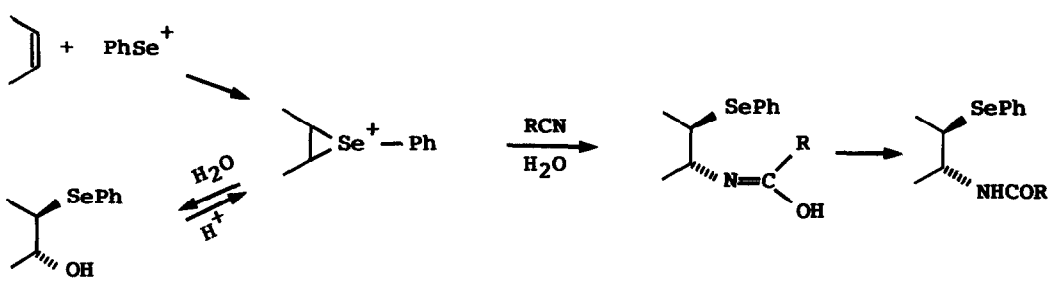
SCHEME 1

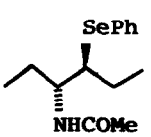


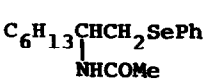
RESULTS AND DISCUSSION

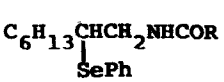
The amidoselenenylation of alkenes was first reported by Toshimitsu and Uemura.[11] The reaction of PhSeCl with olefins in nitriles, containing CF_3SO_3H and H_2O, afforded β-amidoalkyl phenyl selenides in good yield. Some limitations encountered on this one-pot process were overcome by the use of β-hydroxyalkyl phenyl selenides as starting materials.[12] Electron-rich olefins, which do not react under the conditions reported above, gave the amidoselenenylation products when β-methoxyalkyl 2-pyridyl selenides were employed as starting compounds.[13] Before starting our investigations on unsaturated nitriles we carried out some explorative experiments to see if our method[3] could be employed to effect the amidoselenenylation of alkenes also. We found that the reactions of diphenyl diselenide and ammonium peroxydisulphate with olefins in acetonitrile or propionitrile in the presence of trifluoromethanesulphonic acid and water, at 65 °C for 1 - 2 h, afforded the desired products in good yield. These reactions very likely proceed[11] as indicated in Scheme 2. Using cyclohexene, E-3-hexene and

SCHEME 2









1: R = Me (81%)

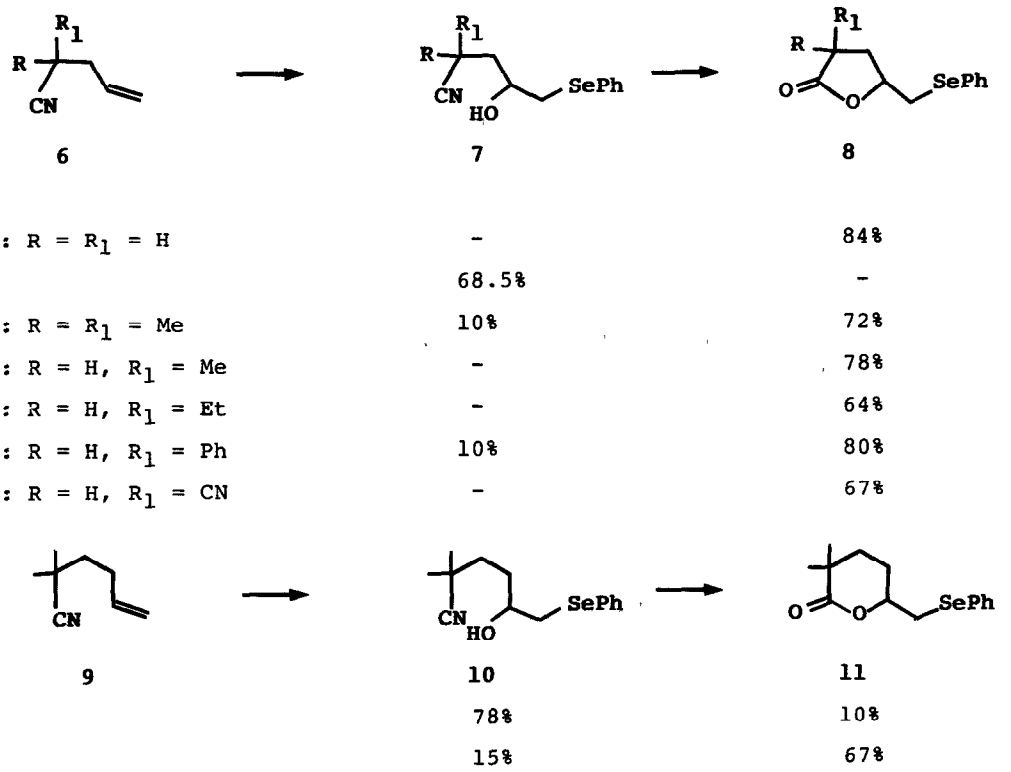
2: R = Et (87%)

3 (78%) 4 (82%) 5 (9%)

1-octene, compounds 1 - 5 were isolated with the yield indicated in parentheses. In agreement with previous observations,[11] the results obtained indicate that the amidoselenenylation is a stereospecific process. With 1-octene the PhSe group was predominantly introduced on the terminal carbon atom, but a small amount of the regioisomer 5 was also isolated.

The reactions of PhSeSePh and $(NH_4)_2S_2O_8$ with olefinic nitriles, in the presence of CF_3SO_3H and H_2O, were carried out in dioxane at 70 °C for 2-4 h. The first substrates investigated were the 4-pentenenitriles **6a - 6f**. The products of these reactions were identified as the (phenylseleno)methyl γ-lactones **8**; in most cases these were accompanied by small amounts of the products **7**, deriving from the hydroxyphenylselenenylation of the carbon-carbon double bond (Scheme 3). Reaction yields of isolated products, after

SCHEME 3



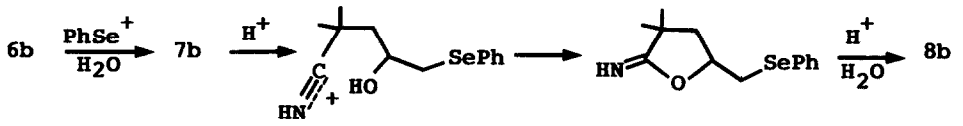
	6	7	8
a: R = R_1 = H		-	84%
		68.5%	-
b: R = R_1 = Me		10%	72%
c: R = H, R_1 = Me		-	78%
d: R = H, R_1 = Et		-	64%
e: R = H, R_1 = Ph		10%	80%
f: R = H, R_1 = CN		-	67%
	9	10	11
		78%	10%
		15%	67%

column chromatography, are also reported in the Scheme. Monitoring the progress of the reactions by tlc, glc, and in some cases by nmr analysis of small aliquots of the reaction mixtures, it was observed that the first products formed were the hydroxy derivatives **7**. These were then gradually consumed and the γ-lactones **8** were produced. In the case of **6a**, when the reaction was stopped after 0.5 h, the only product isolated in 68.5 % yield was the 4-hydroxy-5-(phenylseleno)pentanenitrile **7a**. As indicated by nmr spectra, compounds **8c**, **8d**, and **8e**, were obtained as a 1:1 mixture of cis and trans isomers which could be isolated only in the case of the phenyl derivative **8e**. From the reaction of the allylmalononitrile **6f**, a single isomer (very likely the trans) of the cyano lactone **8f** (67 %) was obtained; the lactone **8a** was also isolated in 20 % yield.

A further example was the reaction of the 2,2-dimethyl-5-hexenenitrile **9** (Scheme 3). In this case, when the reaction was stopped after 2 h at 70 °C, the major reaction product was the 2,2-dimethyl-5-hydroxy-6-(phenylseleno) hexanenitrile **10** (78 %), the δ-lactone **11** being obtained in 10 % yield only. After longer reaction times (20 h), **11** was obtained in 67 % yield, but a small amount of **10** (15 %) was still present. The longer reaction time required in this case can be explained on the basis of the fact that formation of δ-lactones is usually more difficult than that of γ-lactones.

These results seem to indicate that the hydroxy compounds **7** and **10** are the intermediates from which the lactone **8** and **11** originate. A tentative interpretation of the course of these reactions is reported in Scheme 4; the suggested reaction sequence is examplified for compound **6b**. After the fast hydroxyphenylselenenylation reaction of **6b**, it can be suggested that the acid catalyzed hydrolysis of the cyano group in **7b** can take place; this reaction can be helped by intramolecular assistance by the hydroxy group.[14,15] Thus, protonation at the nitrogen atom should produce a cation intermediate, **12**, which can be intramolecularly captured at the carbon atom by the hydroxy group. A cyclic ether bearing an exo-imine substituent, **13**,

SCHEME 4



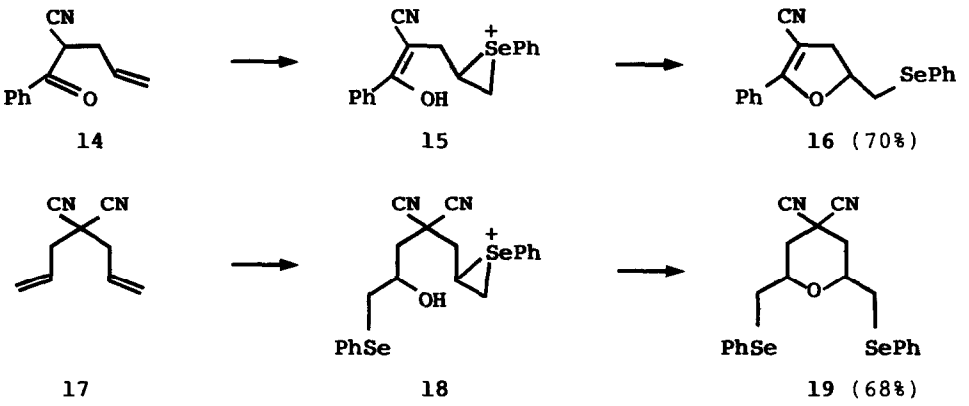
12 13

should thus be formed. Further reaction with acid and water should eventually occur very easily to afford the observed lactone **8b**. Attempts to find experimental evidences for the formation of **13** were carried out by running the reaction of **6b** at room temperature. After a short time the starting product was consumed and the 2,2-dimethyl-4-hydroxy-5-(phenylseleno)pentanenitrile **7b** was formed. After 1 h a second compound was observed by tlc; this product did not correspond to the lactone **8b**. Column chromatography of the reaction mixture afforded some **8b**, the hydroxynitrile **7b** and finally the new product. Ir and nmr spectra can suggest the structure **13** for this compound. Difficulties arose from the fact that this compound was very easily converted into the lactone **8b**. In all the spectra which were recorded absorptions due to the lactone **8b** were also present. Attempted purification of **13** by column chromatography resulted in the almost complete transformation into **8b**.

In some cases the seleno-lactonization process did not take place since other selenium promoted reactions occurred faster. In particular when an acyl or an allyl group were present in the 2 position of the 4-pentenenitrile the carbonyl or the second carbon-carbon double bond became involved in the reaction. As a result the only process observed in these cases was the seleno-etherification. Examples are reported in Scheme 5. Starting from the 2-benzoyl-4-pentenenitrile **14** the only reaction product was the 3-cyano-4,5-dihydro-2-phenyl-5-[(phenylseleno)methyl]furan **16** (70%). Very likely, in this case the seleniranium cation intermediate, **15**, is

captured by the oxygen atom of the enolic form of the starting ketone.[4]

SCHEME 5



The reaction of the 2-cyano-2-allyl-4-pentenenitrile, 17, afforded the product of seleno-etherification, 19, in 68 % yield. The formation of this compound indicates that in the initially formed hydroxyselenenylation product the addition of phenylselenium cation to the second carbon-carbon double bond, to give the seleniranium cation intermediate 18, is a much faster process than the hydrolysis of the cyano group. The formation of cyclic ethers like 19 has already been observed in the reactions of phenylselenium cations, in the presence of water, with dienes having structures similar to that of compound 17.[4,16] Nmr spectra showed that 19 was a single isomer. The presence of only four signals, due to the aliphatic carbon atoms, in the ^{13}C-nmr spectrum suggests a symmetrical structure in which both the $PhSeCH_2$ groups very likely assume an equatorial position.

The reactions described above and summarized in Scheme 3 represent a new example of the seleno-lactonization process. These ring closure reactions are usually carried out starting from unsaturated carboxylic acids.[1,2,4] The use of unsaturated nitriles as starting products is conceptually interesting and can be of some synthetic importance in several cases, also in view of

the fact that these compounds are very easily available. Moreover, the results obtained in the amidoselenenylation of alkenes and in the seleno-lactonization and seleno-etherification reactions confirm the great versatility of the reaction of diphenyl diselenide and ammonium peroxydisulphate as a simple and convenient way of producing phenylselenium cations in the absence of nucleophilic counter ions.[17,18]

EXPERIMENTAL

Glc analyses and MS spectra were carried out with an HP 5890 gascromatograph (dimethyl silicone capillary column, 12.5 m) equipped with an HP 5971 Mass Selective Detector. The presence of six natural isotopes of selenium leads to highly characteristic groups of picks for selenium containing fragments. The values reported below refer only to the prominent picks; for the ions containing selenium only the pick arising from the selenium-80 isotope is given. Proton and carbon-13 nmr spectra were recorded at 200 and 50.32 MHz, respectively, on a Bruker AC 200 instrument; $CDCl_3$ was used as solvent and TMS as standard. IR spectra were recorded on a Perkin Elmer 1320 spectrophotometer. Elemental analyses were carried out on a Carlo Erba 1106 Elemental Analyzer.

Cyclohexene, E-3-hexene and 1-octene were commercial products and were used without further purifications. 4-Pentenenitrile was prepared as described in the literature.[19] Compounds **6b**, **6c**, **6d**, **6e**, **6f**, **14**, and **17** were obtained from commercial nitriles, RR_1CHCN, by deprotonation with lithium diisopropylamide and reaction of the produced carbanion with allyl bromide, according to the general procedure reported in the literature.[19] 2,2-Dimethyl-5-hexenenitrile **9** was similarly prepared from 2-methylpropanenitrile and 4-bromo-1-butene. All these compounds were fully characterized by proton and carbon-13 nmr spectroscopy.

Amidoselenenylation Reactions. General Procedure.

To a mixture of diphenyl diselenide (6 mmol), ammonium peroxydisulphate (6 mmol) and the alkene (10 mmol) in CH_3CN or CH_3CH_2CN (10 ml) a solution of CF_3SO_3H (20 mmol) in H_2O (1 ml) was added. The resulting mixture was stirred at 65 °C. The progress of the reaction was monitored by tlc. After 1-2 h the reaction mixture was poured on water and extracted with chloroform. The organic layer was washed with a solution of sodium carbonate and with water and then dried and evaporated. The reaction products were obtained in pure form after column chromatography on silica gel using chloroform as eluant. Reaction yields are indicated in Scheme 2. Physical and spectral data of compounds 1-5 have already been reported in the literature.[11]

Reactions of Unsaturated Nitriles with Phenylselenium Cations. General Procedure.

To a mixture of diphenyl diselenide (6 mmol), ammonium peroxydisulphate (6 mmol) and the olefinic nitrile (10 mmol) in dioxane (10 ml) a solution of CF_3SO_3H (20 mmol) in H_2O (1 ml) was added. In the reaction of 17, 12 mmol of PhSeSePh and of $(NH_4)_2S_2O_8$ were employed. The resulting mixture was stirred at 70 °C. The progress of the reaction was monitored by tlc, glc and in some cases by nmr. After 2-4 h the reaction mixture was poured on water and extracted with chloroform. In the cases of the reactions of **6a** and **9**, carried out to obtain compounds **7a** and **11**, respectively, the reaction times were decreased to 0.5 h and increased to 20 h, respectively. After washing with sodium carbonate and water the organic layer was dried and evaporated. The residue was chromatographed on silica gel using chloroform or methylene chloride or a mixture of light petroleum and ether (85 : 15) as eluant. Reaction yields are given in Schemes 3 and 5. Compounds **8a** and **16** have already been described in the literature.[4] Physical and spectral data of all the other reaction products are given below.

4-Hydroxy-5-(phenylseleno)pentanenitrile, 7a. Oil. IR 3440 (br), 2240 cm^{-1}. ^1H NMR δ 7.6 - 7.45 (m, 2 H), 7.4 - 7.2 (m, 3 H), 3.85 - 3.6 (m, 1 H), 3.1 (dd, 1 H, J=4.0 and 13.2 Hz), 2.88 (dd, 1 H, J=8.0 and 13.2 Hz), 2.7 br (s, 1 H), 2.5 (t, 2 H, J=7.2 Hz), 2.0 - 1.65 (m, 2 H). ^{13}C NMR δ132.5, 128.9, 127.0, 119.4, 68.1, 35.3, 31.4, 13.3. MS m/e 255 (68), 171 (49), 158 (100), 157 (58), 117 (8), 91 (84), 78 (40), 77 (39), 51 (21). Anal. Calcd. for $C_{11}H_{13}NOSe$: C, 51.98; H, 5.15; N, 5.51. Found: C, 52.13; H, 5.05; N, 5.64.

2,2-Dimethyl-4-hydroxy-5-(phenylseleno)pentanenitrile, 7b. Oil. IR 3500 (br), 2220 cm^{-1}. ^1H NMR δ 7.6 - 7.48 (m, 2 H), 7.53 - 7.2 (m, 3 H), 4.02 - 3.85 (m, 1 H), 3.12 (dd, 1 H, J=4.4 and 12.8 Hz), 2.9 (dd, 1 H, J=8.4 and 12.8 Hz), 2.67 br (d, 1 H, J=3.0 Hz), 1.75 (d, 2 H, J=5.9 Hz), 1.41 (s, 3 H), 1.36 (s, 3 H). ^{13}C NMR δ 133.2, 129.3, 128.9, 127.6, 125.0, 67.6, 46.7, 37.6, 31.2, 27.5, 27.3. MS m/e 283 (69), 172 (100), 157 (60), 91 (66), 78 (32), 77 (38), 69 (20), 55 (29), 43 (59), 41 (35). Anal. Calcd. for $C_{13}H_{17}NOSe$: C, 55.32; H, 6.07; N, 4.96. Found: C, 54.91; H, 6.19; N, 4.83.

Dihydro-3,3-dimethyl-5-[(phenylseleno)methyl]-2(3H)-furanone, 8b. Oil.[4] IR 1770 cm^{-1}. ^1H NMR δ 7.6 - 7.48 (m, 2 H), 7.35 - 7.2 (m, 3 H), 4.58 (dddd, 1 H, J=5.2, 6.0, 7.5 and 9.7 Hz), 3.28 (dd, 1 H, J=5.2 and 12.7 Hz), 3.02 (dd, 1 H, J=7.5 and 12.7 Hz), 2.28 (dd, 1 H, J=6.0 and 12.8 Hz), 1.8 (dd, 1 H, J=9.7 and 12.8 Hz), 1.26 (s, 3 H), 1.22 (s, 3 H). ^{13}C NMR δ 180.7, 132.7, 129.0, 128.8, 127.2, 75.3, 42.9, 40.2, 31.8, 24.7, 24.3. MS m/e 284 (54), 171 (15), 158 (22), 157 (17), 127 (11), 113 (36), 91 (22), 85 (100), 77 (17), 57 (20), 55 (28), 43 (43), 41 (25). Anal. Calcd. for $C_{13}H_{16}O_2Se$: C, 55.13; H, 5.69. Found: C, 55.40; H, 5.81.

The reaction of **6b** was carried out at room temperature also. Tlc analysis of the reaction mixture showed that after 1 h the starting product was consumed and that the lactone **8b** was not yet formed. Together with some hydroxy derivative **7b** a second product was present. Column chromatography of the reaction mixture afforded **8b**, **7b** and the new compound, which was slightly contaminated by **8b**. The infrared spectrum of this product showed absorptions at 3290 (br) and at 1680 cm^{-1}. Proton and carbon-13 nmr spectra

gave the following results: ^{1}H NMR δ 7.6 - 7.48 (m, 2 H), 7.35 - 7.25 (m, 3 H), 4.7 br (s, 1 H), 4.5 (dddd, 1 H, J=5.5, 5.7, 7.3 and 10.0 Hz), 3.25 (dd, 1 H, J=5.5 and 12.6 Hz), 2.98 (dd, 1 H, J=7.3 and 12.6 Hz), 2.16 (dd, 1 H, J=5.7 and 12.6 Hz), 1.74 (dd, 1 H, J=10.0 and 12.6 Hz), 1.3 (s, 3 H), 1.24 (s, 3 H). ^{13}C NMR δ 178.4, 135.4, 133.2, 129.2, 127.4, 75.7, 44.9, 40.8, 26.9, 26.2. On the basis of these spectral properties structure 13 was tentatively assigned to this compound. On standing or on attempted purification by column chromatography this compound was almost completely transformed into the lactone 8b.

Dihydro-3-methyl-5[(phenylseleno)methyl]-2(3H)-furanone, 8c. Oil. IR 1765 cm^{-1}. ^{1}H NMR; from the spectrum of the mixture the absorptions due to the two isomers could be distinguished with the help of decoupling experiments. Trans, δ 7.60 - 7.45 (m, 2 H), 7.35 - 7.20 (m, 3 H), 4.63 (dddd, 1 H, J=4.6, 4.6, 7.9 and 8.3 Hz), 3.22 (dd, 1 H, J=4.6 and 13.5 Hz) 2.95 (dd, 1 H, J=8.3 and 13.5 Hz), 2.68 (ddq, 1 H, J=7.3, 7.9 and 9.0 Hz), 2.22 (ddd, 1 H, J=4.6, 9.0 and 13.1 Hz), 2.02 (ddd, 1 H, J=7.9, 7.9 and 13.1 Hz), 1.25 (d, 3 H, J=7.3 Hz). Cis, δ 7.60 - 7.45 (m, 2 H), 7.35 - 7.20 (m, 3 H), 4.47 (dddd, 1 H, J=5.2, 5.2, 8.0 and 10.5 Hz), 3.29 (dd, 1 H, J=5.2 and 13.0 Hz), 2.98 (dd, 1 H, J=8.0 and 13.0 Hz), 2.64 (ddq, 1 H, J=7.3, 8.5 and 10.5 Hz), 2.60 (ddd, 1 H, J=5.2, 8.5 and 15.6 Hz), 1.46 (ddd, 1 H, J=10.5, 10.5 and 15.6 Hz), 1.25 (d, 3 H, J=7.3 Hz). ^{13}C NMR δ 179.0, 178.4, 133.1, 129.3, 129.0, 127.5, 77.0, 76.7, 37.1, 35.9, 34.9, 33.8, 31.8, 31.7, 15.8, 15.0. MS m/e 270 (68), 171 (23), 158 (30), 157 (21), 113 (20), 99 (100), 91 (40), 77 (25), 61 (61), 43 (77), 41 (42). Anal. Calcd. for $C_{12}H_{14}O_2Se$: C, 53.54; H, 5.24. Found: C, 52.92; H, 5.11.

Dihydro-3-ethyl-5-[(phenylseleno)methyl]-2(3H)-furanone, 8d. Oil. IR 1760 cm^{-1}. ^{1}H NMR δ 7.6 - 7.45 (m, 4 H), 7.3 - 7.15 (m, 6 H), 4.7 - 4.56 (m, 1 H), 4.56 - 4.4 (m, 1 H), 3.3 (dd, 1 H, J=5.1 and 12.7 Hz), 3.23 (dd, 1 H, J=4.85 and 12.9 Hz), 3.01 (dd, 1 H, J=4.2 and 12.9 Hz), 2.96 (dd, 1 H, J=4.7 and 12.7 Hz), 2.7 - 2.45 (m, 3 H), 2.3 - 2.0 (m, 2 H), 2.0 - 1.7 (m, 2 H), 1.7 - 1.35 (m, 3 H), 0.96 (t, 3 H, J=7.4 Hz), 0.95 (t, 3 H, J=7.4 Hz). ^{13}C

NMR δ 178.3, 177.7, 133.0, 129.1, 128.8, 127.4, 77.0, 42.2, 40.4, 34.2, 32.3, 31.8, 31.7, 23.8, 23.1, 11.3. MS m/e 284 (63), 171 (18), 158 (31), 157 (24), 127 (23), 113 (100), 93 (14), 91 (36), 85 (38), 77 (26), 67 (32), 57 (27), 55 (33), 43 (70), 41 (37). Anal. Calcd. for $C_{13}H_{16}O_2Se$: C, 55.13; H, 5.69. Found: C, 55.28; H, 5.84.

2-Phenyl-4-hydroxy-5-(phenylseleno)pentanenitrile, 7e. Oil. IR 3450 (br), 2240 cm^{-1}. ^1H NMR δ 7.6 - 7.45 (m, 2 H), 7.4 - 7.15 (m, 8 H), 4.18 (dd, 1 H, J=4.6 and 11.3 Hz), 4.02 (dddd, 1 H, J=2.6, 4.1, 8.3 and 10.3 Hz), 3.08 (dd, 1 H, J=4.1 and 12.8 Hz), 2.86 (dd, 1 H, J=8.3 and 12.8 Hz), 2.8 br (s, 1 H), 2.1 (ddd, 1 H, J=2.6, 11.3 and 13.8 Hz), 1.9 (ddd, 1 H, J=4.6, 10.3 and 13.8 Hz) ^{13}C NMR δ 135.8, 133.3, 129.3, 129.1, 128.0, 127.6, 127.1, 120.3, 67.5, 42.6, 36.5, 34.4. MS m/e 331 (20), 184 (37), 174 (24), 171 (45), 156 (100), 129 (92), 116 (55), 91 (79), 78 (34), 77 (43), 51 (21), 43 (22). Anal. Calcd. for $C_{17}H_{17}NOSe$: C, 61.82; H, 5.19; N, 4.24. Found: C, 61.67; H, 5.15; N, 4.37.

Dihydro-3-phenyl-5-[(phenylseleno)methyl]-2(3H)-furanone, 8e. Trans. Mp 59 - 61 °C. IR 1730 cm^{-1}. ^1H NMR δ 7.60 - 7.45 (m, 2 H), 7.35 - 7.15 (m, 8 H), 4.82 - 4.68 (m, 1 H), 3.92 (t, 1 H, J=8.5 Hz), 3.28 (dd, 1 H, J=4.85 and 12.8 Hz), 3.04 (dd, 1 H, J=8.1 and 12.8 Hz), 2.5 (dd, 2 H, J=6.4 and 8.5 Hz). ^{13}C NMR δ 176.2, 136.8, 133.1, 129.3, 128.8, 127.6, 127.4, 77.2, 45.3, 35.7, 31.7. MS m/e 332 (35), 184 (20), 175 (40), 171 (16), 157 (47), 131 (53), 129 (100), 115 (16), 105 (55), 103 (24), 91 (85), 77 (32), 51 (14), 43 (16). Anal. Calcd. for $C_{17}H_{16}O_2Se$: C, 61.64; H, 4.87. Found: C, 61.52; H, 4.69. Cis. Oil. IR 1730 cm^{-1}. ^1H NMR δ 7.65 - 7.5 (m, 2 H), 7.45 - 7.2 (m, 8 H), 4.65 (dddd, 1 H, J=4.9, 5.5, 7.8 and 10.2 Hz), 3.86 (dd, 1 H, J=8.8 and 12.8 Hz), 3.38 (dd, 1 H, J=4.9 and 12.8 Hz), 3.1 (dd, 1 H, J=7.8 and 12.8 Hz), 2.85 (ddd, 1 H, J=5.5, 8.8 and 12.8 Hz), 2.13 (ddd, 1 H, J=10.2, 12.8 and 12.8 Hz). ^{13}C NMR δ 180.7, 136.3, 133.3, 129.4, 128.8, 128.0, 127.6, 77.1, 47.2, 37.3, 31.7. MS m/e 332 (35), 171 (10), 157 (13), 131 (100), 105 (37), 91 (56), 77 (21), 43 (16). Found: C, 62.08; H, 4.95.

Dihydro-3-cyano-5-[(phenylseleno)methyl]-2(3H)-furanone, 8f. Oil. IR 2250,

1790 cm^{-1}. ^1H NMR δ 7.6 - 7.45 (m, 2 H), 7.4 - 7.2 (m, 3 H), 4.63 (dddd, 1 H, J=4.8, 5.75, 8.0 and 9.6 Hz), 3.74 (dd, 1 H, J=9.2 and 11.8 Hz), 3.35 (dd, 1 H, J=4.8 and 13.1 Hz), 3.08 (dd, 1 H, J=8.0 and 13.1 Hz), 2.88 (ddd, 1 H, J=5.75, 9.2 and 13.1 Hz), 2.28 (ddd, 1 H, J=9.6, 11.8 and 13.1 Hz). ^{13}C NMR δ 167.3, 133.5, 133.2, 129.5, 128.1, 114.6, 78.8, 33.2, 32.8, 30.7. MS m/e 281 (99), 171 (100), 158 (57), 157 (62), 93 (40), 91 (99), 78 (28), 77 (42), 51 (24), 43 (14). Anal. Calcd. for $C_{12}H_{11}NO_2Se$: C, 51.44; H, 3.96; N, 5.00. Found: C, 51.66; H, 4.07; N, 5.12.

2,2-Dimethyl-5-hydroxy-6-(phenylseleno)hexanenitrile, 10. Oil. IR 3450 (br), 2215 cm^{-1}. ^1H NMR δ 7.6 - 7.45 (m, 2 H), 7.35 - 7.2 (m, 3 H), 3.7 - 3.55 (m, 1 H), 3.1 (dd, 1 H, J=3.8 and 13.1 Hz), 2.9 (dd, 1 H, J=8.5 and 13.1 Hz), 2.65 br (s, 1 H), 1.8 - 1.4 (m, 4 H), 1.3 (s, 6 H). ^{13}C NMR δ 132.7, 129.1, 128.9, 127.0, 124.5, 69.4, 36.7, 36.3, 31.9, 31.8, 26.4, 26.0. MS m/e 297(40), 172 (100), 158 (57), 157 (51), 95 (19), 91 (40), 81 (23), 78 (23), 77 (25), 43 (40). Anal. Calcd. for $C_{14}H_{19}NOSe$: C, 56.76; H, 6.46; N, 4.73. Found: C, 56.58; H, 6.31; N, 4.80.

Tetrahydro-3,3-dimethyl-6-[(phenylseleno)methyl]-2H-pyran-2-one. 11. Oil. IR 1710 cm^{-1}. ^1H NMR δ 7.6 - 7.45 (m, 2 H), 7.35 - 7.2 (m, 3 H), 4.5 - 4.35 (m, 1 H), 3.25 (dd, 1 H, J=4.6 and 12.8 Hz), 3.05 (dd, 1 H, J=7.7 and 12.8 Hz), 2.15 - 2.0 (m, 1 H), 1.85 - 1.6 (m, 3 H), 1.3 (s, 6 H). ^{13}C NMR δ 176.3, 132.7, 129.5, 129.1, 127.2, 96.0, 80.2, 37.8, 34.0, 32.6, 27.6, 27.4, 25.2. MS m/e 298 (42), 171 (7), 157 (16), 127 (24), 99 (45), 95 (10), 91 (16), 81 (100), 77 (15), 55 (24), 43 (44), 41 (23). Anal. Calcd. for $C_{14}H_{18}O_2Se$: C, 56.57; H, 6.10. Found: C, 56.44; H, 5.97.

2,5-Bis[(phenylseleno)methyl]-4,4-dicyanotetrahydropyran, 19. Oil. IR 2240 cm^{-1}. ^1H NMR δ 7.6 - 7.45 (m, 2 H), 7.35 - 7.2 (m, 3 H), 3.8 (dddd, 1 H, J=1.6, 5.7, 6.4 and 11.3 Hz), 3.05 (dd, 1 H, J=5.7 and 12.8 Hz), 2.9 (dd, 1 H, J=6.4 and 12.8 Hz), 2.48 (dd, 1 H, J=1.6 and 13.2 Hz), 1.88 (dd, 1 H, J=11.3 and 13.2 Hz). ^{13}C NMR δ 135.5, 133.4, 128.9, 127.6, 115.0, 114.3, 73.0, 37.6, 31.6, 30.9. Anal. Calcd. for $C_{21}H_{20}N_2OSe_2$: C, 53.18; H, 4.25; N, 5.91. Found: C, 53.10; H, 4.40; N, 6.06.

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REFERENCES AND NOTES

1) Paulmier, C. "Selenium Reagents and Intermediates in Organic Synthesis", Pergamon Press: Oxford, 1986.
2) Liotta, D. "Organoselenium Chemistry", Wiley Interscience: New York, 1987.
3) Tiecco, M.; Testaferri, L.; Tingoli, M.; Bartoli, D. Tetrahedron Lett. 1989, 30, 1417.
4) Tiecco, M.; Testaferri, L.; Tingoli, M.; Bartoli, D.; Balducci, R. J. Org. Chem., submitted for publication.
5) Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Bartoli, D. Tetrahedron 1988, 44, 2261.
6) Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Bartoli, D. Tetrahedron 1988, 44, 2273.
7) (a) Nicolau, K.C.; Claremon, D.A.; Barnette, W.E.; Seitz, S.P. J. Am. Chem. Soc. 1979, 101, 3704. (b) Nicolau, K.C.; Petatis, N.A.; Claremon, D.A. Tetrahedron 1985, 41, 4835. (c) Jackson, W.P.; Ley, S.V.; Morton, J.A. J. Chem. Soc., Chem. Commun. 1980, 1028.
8) (a) Schmid, G.H.; Garratt, D.G. Tetrahedron Lett. 1975, 3991. (b) Remion, J.; Krief, A. Tetrahedron Lett. 1976, 3743. (c) Jackson, W.P.; Ley, S.V.; Whittle, A.J. J. Chem Soc., Chem. Commun. 1980, 1173.
9) Murata, S.; Suzuki, T. Chem. Lett. 1987, 849.
10) Murata, S.; Suzuki, T. Tetrahedron Lett. 1987, 28, 4297, 4415.
11) Toshimitsu, A.; Aoai, T.; Owada, H.; Uemura, S.; Okano, M. J. Org. Chem. 1981, 46, 4727.
12) Toshimitsu, A.; Hayashi, G.; Terao, K.; Uemura, S. J. Chem. Soc., Perkin Trans I 1986, 343.
13) Toshimitsu, A.; Hayashi, G.; Terao, K.; Uemura, S. J. Chem. Soc., Perkin Trans I 1988, 2113.
14) Balahura, R.J.; Purcell, W.L. Inorg. Chem. 1981, 20, 4159.
15) Tiecco, M.; Tingoli, M.; Testaferri, L.; Bartoli, D. Synth. Commun., submitted for publication.
16) Toshimitsu, A.; Aoai, T.; Owada, H.; Uemura, S.; Okano, M. Tetrahedron 1985, 41, 5301.
17) The oxidation of PhSeSePh with $S_2O_8^{--}$ can be also used to effect the alkoxyselenenylation of alkynes and of enolizable ketones. In these cases, however, the reaction proceeds further to afford the products of alkoxydeselenenylation. This represents a convenient method to convert alkynes and methyl ketones into α-keto acetals. (a) Tiecco, M.; Testaferri, L.; Tingoli, M.; Bartoli, D.; Chianelli, D. "Organic Free Radicals"; Fischer, H.; Heimgartner, H., Eds; Springer Verlag: Berlin, 1988, p. 209. (b) Tiecco, M.; Testaferri, L.; Tingoli, M. "Free Radicals in Synthesis and Biology"; Minisci, F., Ed.; Kluwer Academic Publishers: Dordrecht, 199, p. 253.
18) In a similar way, oxidation of diaryl disulphides with ammonium peroxydisulphate can be used as a convenient way to produce arylsulphenyl cations. Unpublished results from this laboratory.
19) Toshimitsu, A.; Terao, K.; Uemura, S. J. Org. Chem. 1986, 51, 1724.