pink supernatant liquid decanted off, and CH_2Cl_2 (20 cm^3) added, and the organics were washed repetedly with dilute HCl. The clear CH_2Cl_2 layer was washed with water and dried (Na_2SO_4) and the solvent removed under reduced pressure to give a white solid. Recrystallization from CH_2Cl_2–Et_2O yielded white crystalline **30** (63 mg, 85%): mp >250 °C (CH_2Cl_2–Et_2O); IR (KBr) ν 1255 s (C═C), 1188 s (P═O) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.07 (3 H, s, OMe), 3.71 (3 H, s, OMe), 6.79 (1 H, dd, $J_{4,5}$ = 9.0 Hz, J_{PH} = 5.8 Hz, 4-H), 6.91 (1 H, d, $J_{4,5}$ = 9.0 Hz, 5-H), 7.13–7.17 (4 H, m, Ph-*m*), 7.21–7.25 (2 H, m, Ph-*p*), 7.39–7.44 (4 H, m, Ph-*m*), 7.45–7.50 (2 H, m, Ph-*p*), 7.63–7.69 (4 H, m, Ph-*o*), 7.82–7.89 (4 H, m, Ph-*o*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 51.6 (OMe), 53.9 (OMe), 56.2 (OMe), 58.4 (OMe), 110.3 (d, J_{PC} = 7 Hz, 4-C), 112.8 (5-C), 112.9 (d, J_{PC} = 8 Hz, 4-C), 115.3 (5-C), 120.3 (d, J_{PC} = 105 Hz, 2-C), 126.1–135.2 (Ph), 137.6 (d, J_{PC} = 111 Hz, Ph-*i*), 152.1 (br, 3-C), 153.7 (br, 6-C), 1-C not detected, 3:1 mixture of species; ^{31}P NMR (101.3 MHz, $CDCl_3$) δ 26.2 (P═O); MS 675 $(M + 1)^+$. Anal. Calcd for $C_{40}H_{36}O_6P_2$: C, 71.2; H, 5.4. Found: C, 71.0; H, 5.65.

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Registry No. **10**, 13291-46-8; **11**, 72666-56-9; **12**, 136202-00-1; **13**, 136202-01-2; **14**, 136202-02-3; **18**, 85417-48-7; **19**, 136202-03-4; **20**, 136202-04-5; **21**, 136202-05-6; **22**, 136202-06-7; **23**, 136202-07-8; **24**, 136202-08-9; **25**, 136202-09-0; **26**, 136202-10-3; **27**, 136202-11-4; **28**, 136202-12-5; **30**, 136202-13-6; $Ph_2P(O)H$, 4559-70-0; Ph_2S_2, 882-33-7; $Ph_2P(O)Cl$, 1499-21-4; (*S*)-PhCHMeNH$_2$, 2627-86-3; *p*-benzoquinone, 106-51-4; 2-diphenylthiophosphinoylquinhydrol, 54573-03-4; [6-^{2}H](2,5-dimethoxyphenyl)diphenylphosphine, 136201-98-4; [4-^{2}H](2,5-dimethoxyphenyl)diphenylphosphine sulfide, 136201-99-5; 2,3-dimethoxybenzaldehyde, 86-51-1.

Novel Azido-phenylselenenylation of Double Bonds. Evidences for a Free Radical Process

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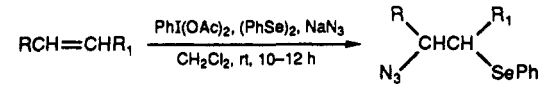
A simple and mild azido-phenylselenenylation of terminal alkenes, which proceeds with complete anti-Markovnikov regioselectivity, has been developed. This reaction occurs when the alkenes are treated with (diacetoxyiodo)benzene, sodium azide, and diphenyl diselenide in dichloromethane at room temperature. The observed regioselectivity can be explained by assuming that the addition process is initiated by azido radicals. This was further supported by the results obtained starting from 1,6-heptadiene and from β-pinene. Under the same conditions, efficient azido-phenylselenenylation of symmetrical olefins, 3,4-dihydro-2*H*-pyran, methyl acrylate, and vinyl crotonate can also be effected.

It is well established that addition to unsymmetrical olefins initiated by electrophilic phenylselenium species proceeds through the formation of seleniranium intermediates which, in the presence of external or internal nucleophiles, usually affords anti adducts with prevalent Markovnikov orientation.[1] We have recently reported the in situ generation of an electrophilic phenylselenenylating agent that reacts with olefins to effect methoxy-, hydroxy-, and amidoselenenylation or selenium-induced ring closure reactions.[2] This strong phenylselenenylating agent is produced when diphenyl diselenide is allowed to react with ammonium peroxydisulfate in different solvents. In some cases, by using an excess of ammonium peroxydisulfate and catalytic amounts of diphenyl diselenide in methanol, the unsaturated compounds undergo alkoxyselenenylation followed by alkoxydeselenenylation reactions.[3]

Scheme I

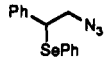
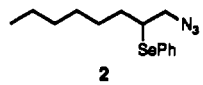
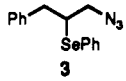
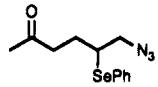
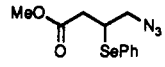
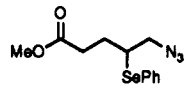
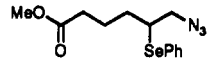
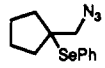
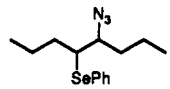
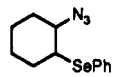


In all the examples we have described, the trapping of the selenium-containing intermediates and the replacement of the phenylselenium group were always effected by oxygen-centered nucleophiles. An experiment was carried out, using styrene as substrate, and effecting the oxidation of diphenyl diselenide with ammonium peroxydisulfate in the presence of sodium azide in an attempt to extend the use of this methodology to nitrogen nucleophiles. A complex reaction mixture was obtained in this case and the expected product of azido-phenylselenenylation could be obtained in very poor yield. In a parallel investigation we have recently observed that electrophilic phenylselenium species can be produced from diphenyl diselenide, under much milder conditions, by using hypervalent iodine reagents.[4] Application of this procedure to the azido-phenylselenenylation of styrene, using sodium azide, in dichloromethane, gave the expected product in excellent yield. However, careful examination of the spectral data of this compound demonstrated that the addition took place with an unexpected regioselectivity, the azido group being bonded to the terminal carbon atom.

(1) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*, Pergamon Press: Oxford, 1986; p 185.
(2) (a) Tiecco, M.; Testaferri, L.; Tingoli, M.; Bartoli, D.; Balducci, R. *J. Org. Chem.* **1990**, *55*, 429. (b) Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Bartoli, D. *Tetrahedron* Lett. **1989**, *30*, 1417. (c) Unpublished results from this laboratory.
(3) (a) Tiecco, M.; Testaferri, L.; Tingoli, M. *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; Kluwer Academic: Dordrecht, 1989; p 253. (b) Tiecco, M.; Testaferri, L; Tingoli, M.; Chianelli, D.; Bartoli, D. *Tetrahedron* **1988**, *44*, 2273. Tiecco, M.; Testaferri, L.; Tingoli, M.; Bartoli, D. *J. Org. Chem.* **1990**, *55*, 4523. Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Bartoli, D. *J. Org. Chem.* **1991**, *56*, 4529. Tiecco, M.; Testaferri, L.; Tingoli, M.; Bartoli, D.; Marini, F. *J. Org. Chem.* **1991**, *56*, 5207.
(4) Unpublished results from this laboratory.

0022-3263/91/1956-6809$02.50/0

Table I. Azido-phenylselenenylation of Olefins

entry	substrate	reaction products	yield (%)[a]
1	styrene	 1	82
2	1-octene	 2	78
3	allylbenzene	 3	68
4	5-hexen-2-one	 4	71
5	methyl 3-butenoate	 5	62
6	methyl 4-pentenoate	 6	83
7	methyl 5-hexenoate	 7	71
8	methylenecyclopentane	 8	80
9	(*E*)-4-octene	 9[b]	81
10	cyclohexene	 10[c]	79

[a] Calculated on isolated products. [b] 2:1 diastereomeric mixture. [c] 3:1 diastereomeric mixture.

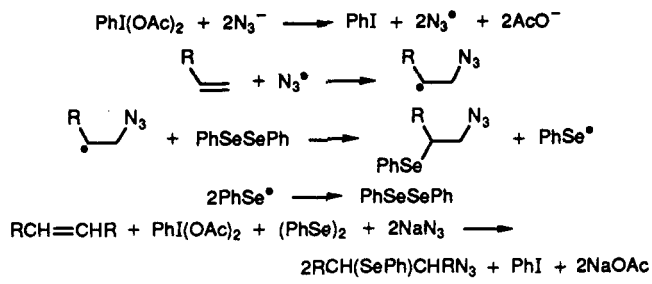
Thus, this new oxidizing system seems to promote the reaction but the observed regioselectivity suggests that electrophilic phenylselenium species are not involved. This azido-phenylselenenylation process apparently proceeds through a reaction pathway that is different from that observed when the reactions are carried out in the presence of oxygen nucleophiles. We report in this paper several examples of azido-selenenylation reactions of terminal and internal alkenes; 1,6-heptadiene, β-pinene, 3,4-dihydro-2*H*-pyran, methyl acrylate, and vinyl crotonate have also been successfully employed as substrates. From the data obtained from these experiments we propose that this new process is initiated by azido radicals.

Results and Discussion

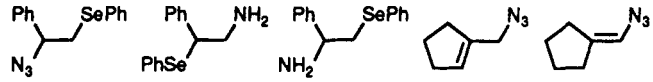
The azido-phenylselenenylation reactions were simply carried out by stirring a mixture of the olefin (5 mmol) with (diacetoxyiodo)benzene (7 mmol), diphenyl diselenide (3 mmol), and sodium azide (12 mmol) in methylene chloride at room temperature (Scheme I). The products obtained and the reaction yields are reported in Table I.

In the case of terminal olefins (entries 1–8) a single regioisomer was obtained after column chromatography. GC-MS analysis of the crude reaction mixtures showed that the other isomer was present in minute amounts (less than 5%) in every case. Structural assignment of compounds 1–8 was based on proton and carbon-13 NMR

Scheme II



spectra. In the case of styrene the other regioisomer **11** could be obtained from the reaction of diphenyl diselenide, sodium azide, and *m*-nitrobenzenesulfonyl peroxide in acetonitrile.[5] Reduction of **1** and **11** with $LiAlH_4$ in THF afforded the amino derivatives **12** and **13**, respectively. The NMR data of compounds **1** and **11**, as well as those of **12** and **13** (see Experimental Section), were in agreement with the proposed structures. Clearcut chemical evidences were obtained from the structure of compound **8** deriving from the azido-phenylselenenylation of methylenecyclopentane. In fact, when **8** was oxidized to the corresponding selenoxide, a spontaneous elimination took place to afford a 3:1 mixture of the two alkenes **14** and **15** (76%), clearly demonstrating that the phenylselenium group in compound **8** was linked to the tertiary carbon atom.



11 **12** **13** **14** **15**

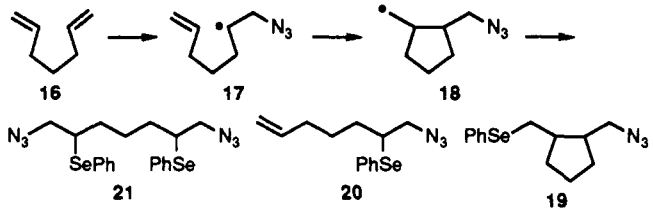
These results indicate that the azido-phenylselenenylation reaction proceeds with high regiospecificity and affords the anti-Markovnikov addition products.

Also reported in Table I are the results obtained with the symmetrical olefins (*E*)-4-ocetene and cyclohexene (entries 9 and 10). GC-MS and NMR analysis of the reaction products, **9** and **10**, respectively, demonstrated that in both cases a mixture of two stereoisomers was obtained, which, however, could not be separated by column chromatography. These results clearly indicate that the presently described azido-phenylselenenylation of alkenes is not a stereospecific process.

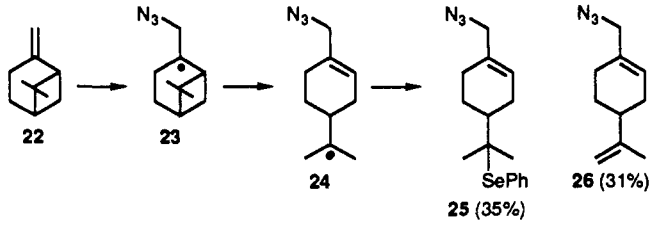
On the basis of its stereochemical course, it is difficult to assume that the process is promoted by the electrophilic phenylselenenylating agent generated from the reaction of $PhI(OAc)_2$ with PhSeSePh. In fact, Hassner and Amarasekara have recently reported that the reaction of alkenes with PhSeCl and NaN_3 in DMSO, which is suggested to involve a seleniranium ion intermediate, proceeds stereospecifically but not regiospecifically.[6] In the present case the addition process clearly proceeds through a completely different reaction pathway, and the results obtained seem to indicate that the azido-phenylselenenylation described in this paper is a free radical reaction. In view of the low oxidation potential of the azido anion (0.78 eV vs SCE[7]), we suggest that the fastest process occurring under the employed reaction conditions is the oxidation of this anion to the corresponding azido radical (Scheme II) by the $PhI(OAc)_2$. Addition of this radical to the double bond should afford a carbon radical that is rapidly trapped by the PhSeSePh to afford the observed addition products and the phenylselenenyl radical. This latter could in principle add to the alkenes and initiate a new radical

(5) Yoshida, M.; Satoh, N.; Kamigata, N. *Chem. Lett.* **1989**, 1433.
(6) Hassner, A.; Amarasekara, A. S. *Tetrahedron Lett.* **1987**, *28*, 5185.
(7) Plsak, V.; Wendt, H. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 481.

Scheme III



Scheme IV

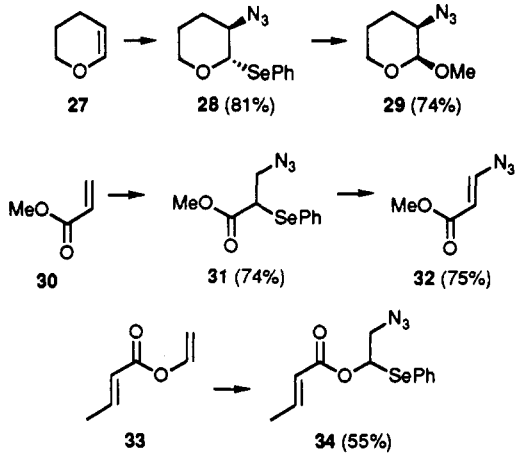


chain reaction from which vicinal bis(phenylselenenyl) derivatives should form. It is well known however that this does not occur since the addition of PhSe radicals to carbon–carbon double bonds is a reversible process.[8] The reasonable fate of the PhSe radicals is their recombination to form diphenyl diselenide.

The reaction sequence proposed in Scheme II clearly explains the stereochemical course of the azido-phenylselenenylation reaction and it also finds support from other results already reported in the literature. It is knwon, in fact, that azido anions can be oxidized to the corresponding radicals by Fe(II)/H_2O_2[9] or by metals, like Pb(IV)[10] or Mn(III),[11] or electrochemically.[12] In every case, it is reported that azido radicals easily add to carbon–carbon double bond to give vicinal diazido derivatives. These compounds were also obtained from the reaction of alkenes with (diacetoxyiodo)benzene and sodium azide in acetic acid; in this case, however, their formation takes place through a completely different mechanism, which does not involve azido radicals.[13]

For further evidence supporting the proposed reaction sequence reported in Scheme II, an experiment was carried out starting from 1,6-heptadiene (**16**) with the expectation that the initially formed carbon radical **17** should cyclize[14,15] to give **18**, which is then trapped by the diphenyl diselenide to eventually afford the cyclopentane derivative **19** (Scheme III). Three products were isolated from this reaction, after flash chromatography, in a 1:1:1 ratio (65%). These were identified as the expected cyclopentane derivative **19** (as a 3:1 mixture of two non-isolated diastereoisomers) and as the open-chain products deriving from the azido-phenylselenenylation of a single double bond, **20**, and of both double bonds, **21** (as a 1:1 mixture of two diastereoisomers). The formation of **19** strongly supports the radical nature of the azido-phenylselenenylation reaction described in this paper. Radicals having structures

Scheme V



similar to that of **17** are known to cyclize with a rate that is on the order of 10^5 s^{-1} and have been extensively used as "radical clocks" to estimate the rate of several radical reactions.[14,15] In the present case the fact that the open-chain products **20** and **21** are formed in considerable amounts indicates that the trapping of carbon radicals by diphenyl diselenide is a fast process, which occurs with a rate comparable to that of the cyclization of **17** to **18**. The results obtained from the reaction carried out on β-pinene (**22**) were in agreement with the known behavior of this substrate toward free radical addition reactions.[16] Compounds **25** and **26** were in fact isolated from this reaction (Scheme IV). In this and in the following schemes reaction yields are reported in parentheses. The structures of these two compounds indicate that the initially formed radical, **23**, suffers the opening of the strained four-membered ring to give the more stable tertiary radical **24**. Cleavage of a carbon–carbon bond β to a carbon-centered radical is a well-known process that readily occurs in the case of cyclopropylmethyl and cyclobutylmethyl radicals to produce the more stable acyclic radicals.[16]

In conclusion, the whole of the results described above seems to indicate that the azido-phenylselenenylation reaction described in the present paper is a radical process that is initiated by azido radicals; all the other possible processes, such as the oxidation of the PhSeSePh by $PhI(OAc)_2$ or the direct electrophilic addition of this hypervalent iodine reagent to the carbon–carbon double bond, are completely suppressed under the reaction conditions employed.[17]

For exploration of applications of this new azido-phenylselenenylation reaction, experiments were carried out starting from some other representative alkene derivatives. An interesting result was obtained from the reaction of 3,4-dihydro-2*H*-pyran (**27**) from which a single product was surprisingly obtained. This was identified as 3-azido-2-(phenylseleno)tetrahydropyran (**28**) (Scheme V). In this case therefore the reaction was not only regiospecific but also surprisingly stereospecific. The trans relationship of the two substituents was established on the basis of the coupling constant (4.3 Hz) measured for the anomeric proton,[18] which appeared as a doublet at 5.38 ppm. Oxidation of **28** with hydrogen peroxide in methanol did not

(8) Back, T. G.; Krishna, M. V. *J. Org. Chem.* **1988**, *53*, 2533.
(9) Minisci, F. *Chim. Ind. (Milan)* **1967**, *49*, 706.
(10) Hugl, H.; Zbiral, E. *Tetrahedron* **1973**, *29*, 759.
(11) Fristad, W. E.; Brandvold, T. A.; Peterson, J. R.; Thompson, S. R. *J. Org. Chem.* **1985**, *50*, 3647.
(12) (a) Schafer, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 158. (b) Kosten, K.; Riemenschneider, P.; Wendt, H. *Isr. J. Chem.* **1979**, *18*, 141. (c) See ref 10.
(13) Moriarty, R. M.; Khosrowshahi, J. S. *Tetrahedron Lett.* **1986**, *27*, 2809.
(14) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.
(15) The use of intramolecular radical rearrangement as "mechanistic probes" provide qualitative evidence that the mechanism under study proceedes via the intermediacy of a free radical. Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206.
(16) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon bonds*; Pergamon Press: Oxford, 1986; p 74, 79, 92.
(17) On the other hand the course of the reaction seems to be influenced by the solvent employed. From an experiment carried out with styrene in acetonitrile, together with 1, a considerable amount of PhCH(OAc)CH_2SePh, clearly deriving from an ionic process,[4] was also formed.
(18) Garratt, D. G. *Can. J. Chem.* **1978**, *56*, 2184.

give the expected elimination product but afforded the 3-azido-2-methoxytetrahydropyran (**29**) in 74% yield. This was not completely unexpected since we have recently observed that geminal alkoxy phenyselenenyl derivatives, upon oxidation with ammonium peroxydisulfate in methanol, give rise to the methoxydeselenenylation products.[19] The anomeric proton in **29** appeared as a doublet at 4.65 ppm with a coupling constant of 3.1 Hz, which is indicative of a cis relationship between the two substituents. Thus the replacement of the PhSe with the MeO group occurred with inversion of configuration.

Owing to its radical nature the azido-phenylselenenylation process occurs with α,β-unsaturated esters also. Starting from methyl acrylate (**30**), the addition product **31** was in fact obtained. Oxidation with H_2O_2 in MeOH easily gave the expected elimination product **32** in 74% yield. Finally, a reaction was carried out with vinyl crotonate (**33**) in order to explore the chemoselectivity of the process. Although the yield of the isolated product was moderate (55%), the reaction selectively involved the more electron-rich carbon–carbon double bond and compound **34** was obtained.

In conclusion, the presently described oxidation of azido anions by (diacetoxyiodo)benzene in methylene chloride, in the presence of diphenyl diselenide, represents a new and very mild method for effecting the regioselective azido-phenylselenenylation of several types of substituted alkenes. Moreover, the products obtained represent very versatile intermediates, which have useful synthetic applications.

Experimental Section

Most of the starting olefinic compounds were commercial products that were used without further purification. 5-Hexenoic acid was prepared by Jones oxidation of the corresponding primary alcohol. The methyl esters were prepared on treating the corresponding acids with ethereal CH_2N_2. Oxidation of selenides **8**, **25**, **28**, and **31** was performed with 30% H_2O_2 in a methanolic solution at 0 °C for 1 h and then at rt for 3 h. Reduction of seleno azides **1** and **11** was realized as described in the literature in almost quantitative yields.[20] Reaction products were identified by proton and carbon-13 NMR spectroscopy, mass spectrometry, and elemental analyses carried out as previously reported.[3] Silica gel 60 (230–400 mesh) was used for flash chromatography.

Azido-phenylselenenylation. General Procedure. A mixture of the olefin (5 mmol), diphenyl diselenide (3 mmol), sodium azide (12 mmol), and (diacetoxyiodo)benzene (7 mmol) in methylene chloride (20 mL) was stirred at rt for 10–12 h. The progress of the reaction was monitored by TLC and GLC. The mixture was poured on 10% aqueous $NaHCO_3$ and extracted with methylene chloride. The organic layer was washed with brine, dried, and evaporated.

The reaction products were obtained in pure form after flash chromatography on silica gel with mixtures of petroleum ether and ether (from 90:10 to 70:30) as eluant. Reaction yields are indicated in Table I and Schemes III and IV. Physical and spectral data of the reaction products are reported below.

2-Azido-1-phenyl-1-(phenylseleno)ethane (1): oil; IR (neat) 2090 cm^{-1}; ^1H NMR δ 7.6–7.45 (m, 2 H), 7.4–7.2 (m, 3 H), 4.38 (dd, 1 H, J = 5.8 and 9.6 Hz), 3.86 (dd, 1 H, J = 9.6 and 12.6 Hz), 3.68 (dd, 1 H, J = 5.8 and 12.6 Hz); ^{13}C NMR δ 138.9, 135.5, 129.1, 128.6, 128.3, 127.7, 126.7, 55.4 (CH_2N_3) 46.3 (CHSePh); MS m/e (rel intensity) 303 (3), 195 (9), 167 (9), 157 (17), 118 (25), 117 (32), 91 (100), 77 (20), 65 (16). Anal. Calcd for $C_{14}H_{13}N_3Se$: C, 55.64; H, 4.34; N, 13.90. Found: C, 55.86; H, 4.32; N, 13.93.

2-Phenyl-2-(phenylseleno)ethanamine (12): mp 65 °C; ^1H NMR δ 7.5–7.35 (m, 2 H), 7.3–7.1 (m, 8 H), 4.2 (t, 1 H, J = 7.3 Hz), 3.16 (q, 1 H, J = 13.2 Hz), 3.19 (q, 1 H, J = 13.4 Hz), 1.3 (bs, 2 H); ^{13}C NMR δ 140.6, 135.0, 128.6, 128.2, 127.6, 127.5, 127.0, 51.6 (CHSePh), 46.6 (CH_2NH_2); MS m/e (rel intensity) 277 (3), 248 (3), 120 (M^+ – PhSe, 100) 118 (8), 91 (26), 78 (7). Anal. Calcd for $C_{14}H_{15}NSe$: C, 60.87; H, 5.47; N, 5.07. Found: C, 60.81; H, 5.47; N, 5.06.

1-Azido-1-phenyl-2-(phenylseleno)ethane (11). Diphenyl diselenide (0.5 mmol) and m-nitrobenzenesulfonyl peroxide (0.5 mmol) in CH_3CN (20 mL) were stirred at 0 °C for 0.5 h; then styrene (1 mmol) in CH_3CN (5 mL) and NaN_3 (1 mmol) were added. The mixture was stirred at rt for 8 h. After usual workup and column chromatography with petroleum ether as eluant, compound 11 was obtained (74% yield):[5] oil, IR (neat) 2100 cm^{-1}; ^1H NMR δ 7.6–7.4 (m, 2 H), 7.4–7.15 (m, 8 H), 4.62 (dd, 1 H, J = 6.5 and 7.9 Hz), 3.23 (dd, 1 H, J = 7.9 and 12.6 Hz), 3.18 (dd, 1 H, J = 6.5 and 12.6 Hz); ^{13}C NMR δ 138.7, 133.3, 129.2, 128.8, 128.6, 127.4, 126.8, 66.0 (CHN_3), 33.9 (CH_2SePh); MS m/e (rel intensity) 303 (6), 275 (7), 171 (29), 157 (36), 104 (87), 91 (100), 65 (15), 51 (36). Anal. Calcd for $C_{14}H_{13}N_3Se$: C, 55.64; H, 4.34; N, 13.90. Found: C, 55.71; H, 4.38; N, 13.84.

1-Phenyl-2-(phenylseleno)ethanamine (13): mp 56 °C; ^1H NMR δ 7.6–7.45 (m, 2 H), 7.3–7.1 (m, 8 H), 4.04 (dd, 1 H, J = 4.1 and 9.3 Hz), 3.22 (dd, 1 H, J = 4.1 and 12.4 Hz), 2.99 (dd, 1 H, J = 9.3 and 12.4 Hz), 1.75 (s, 2 H); ^{13}C NMR δ 144.5, 132.6, 129.9, 128.9, 128.3, 127.2, 126.8, 126.1, 55.2 ($CHNH_2$), 38.2 (CH_2SePh); MS m/e (rel intensity) 277 (1), 172 (19), 106 (M^+ – $PhSeCH_2$, 100), 91 (8), 79 (21). Anal. Calcd for $C_{14}H_{15}NSe$: C, 60.87; H, 5.47; N, 5.07. Found: C, 60.98; H, 5.54; N, 4.98.

1-Azido-2-(phenylseleno)octane (2): oil, IR (neat) 2090 cm^{-1}; ^1H NMR δ 7.6–7.45 (m, 2 H), 7.35–7.1 (m, 3 H), 3.55 (dd, 1 H, J = 4.0 and 16.0 Hz), 3.40 (dd, 1 H, J = 8.0 and 16.0 Hz), 3.28–3.18 (m, 1 H), 1.9–1.15 (m, 13 H); ^{13}C NMR δ 135.2, 133.0, 129.0, 127.9, 55.9, 44.6, 32.4, 31.5, 28.9, 27.4, 22.5, 13.9; MS m/e (rel intensity) 311 (5), 283 (4), 194 (4), 157 (29), 132 (13), 126 (18), 91 (21), 82 (12), 55 (100). Anal. Calcd for $C_{14}H_{21}N_3Se$: C, 54.19; H, 6.82; N, 13.54. Found: C, 54.02; H, 6.80; N, 13.50.

6-Azido-5-(phenylseleno)hexan-2-one (4): oil; IR (neat) 2090 and 1700 cm^{-1}; ^1H NMR δ 7.6–7.45 (m, 2 H), 7.3–7.15 (m, 3 H), 3.53 (dd, 1 H, J = 5.5 and 12.5 Hz), 3.41 (dd, 1 H, J = 7.1 and 12.5 Hz), 3.2–3.1 (m, 1 H), 2.66 (t, 2 H, J = 8.6 Hz), 2.05 (s, 1 H), 1.8–1.6 (m, 2 H); ^{13}C NMR δ 206.5, 134.7, 132.6, 128.8, 127.6, 55.6, 43.6, 32.0, 29.3, 26.1; MS m/e (rel intensity) 296 (1), 250 (5), 169 (17), 157 (20), 112 (6), 91 (8), 83 (12), 78 (25), 68 (20), 43 (100). Anal. Calcd for $C_{12}H_{15}N_3OSe$: C, 48.66; H, 5.10; N, 14.19. Found: C, 48.56; H, 5.07; N, 14.16.

Methyl 3-azido-2-(phenylseleno)propanoate (31): oil; IR (neat) 2110 and 1730 cm^{-1}; ^1H NMR δ 7.65–7.55 (m, 2 H), 7.4–7.22 (m, 3 H), 3.8–3.5 (m, 6 H); ^{13}C NMR δ 171.0, 135.9, 135.8, 129.1, 129.0, 52.2, 52.0, 41.0. MS m/e (rel intensity) 285 (11), 256 (7), 169 (26), 157 (57), 117 (33), 91 (25), 77 (53), 59 (11), 45 (100. Anal. Calcd for $C_{10}H_{11}N_3O_2Se$: C, 42.27; H, 3.90; N, 14.79. Found: C, 42.34; H, 4.98; N, 14.82.

Methyl 3-azido-(*E*)-acrylate (32): mp 49–52 °C; IR (neat) 2100 and 1700 cm^{-1}; ^1H NMR δ 7.34 (d, 1 H, J = 13.4 Hz), 5.65 (d, 1 H, J = 13.4 Hz), 3.72 (m, 3 H); ^{13}C NMR δ 165.8, 144.1, 108.6, 51.2; MS m/e (rel intensity) 99 (M^+ – 28, 1), 68 (60), 59 (100), 55 (9), 54 (9). Anal. Calcd for $C_4H_5N_3O_2$: C, 37.80; H, 3.97; N, 33.06. Found: C, 37.87, H, 4.08; N, 33.14.

***trans*-3-Azido-2-(phenylseleno)tetrahydropyran (28)**: oil, IR (neat) 2090 cm^{-1}; ^1H NMR δ 7.65–7.55 (m, 2 H), 7.3–7.1 (m, 3 H), 5.36 (d, 1 H, J = 4.3 Hz), 4.18–4.02 (m, 1 H), 3.8–3.58 (m, 2 H), 2.2–1.4 (m, 4 H); ^{13}C NMR δ 134.0, 128.9, 128.6, 127.6, 85.01, 76.3, 64.2, 26.3, 21.6; MS m/e (rel intensity) 282 (M^+ – 1, 2), 156 (30), 126 (35), 78 (36), 71 (13), 68 (100), 51 (15). Anal. Calcd for $C_{11}H_{13}N_3OSe$: C, 46.82; H, 4.64; N, 14.89. Found: C, 46.77; H, 4.60; N, 14.81.

***cis*-3-Azido-2-methoxytetrahydropyran (29)**: oil; IR (neat) 2090 cm^{-1}; ^1H NMR δ 4.65 (d, 1 H, J = 3.1 Hz), 3.8–3.65 (m, 1 H), 3.6–3.4 (m, 4 H), 3.25–3.1 (m, 1 H), 2.1–1.65 (m, 4 H); ^{13}C NMR δ 98.9, 58.9, 58.1, 54.9, 24.3, 22.9; MS m/e (rel instensity) 129 (M^+ – 28, 1), 98 (1), 71 (14), 69 (29), 68 (32), 61 (41), 43 (9), 42 (100). Anal. Calcd for $C_6H_{11}N_3O_2$: C, 45.85; H, 7.05; N, 26.74. Found: C, 45.91; H, 7.14; N, 26.81.

1-(Azidomethyl)-1-(phenylseleno)cyclopentane (8): oil; IR (neat) 2100 cm^{-1}; ^1H NMR δ 7.7–7.55 (m, 2 H), 7.45–7.2 (m, 3 H), 3.49 (bs, 2 H), 2.0–1.6 (m, 8 H); ^{13}C NMR δ 137.7, 128.9, 128.8, 127.7, 60.1, 57.5, 36.3, 24.4; MS m/e (rel intensity) 281 (7), 253

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(1), 158 (84), 96 (25), 81 (54), 69 (48), 67 (81), 41 (100). Anal. Calcd for $C_{12}H_{15}N_3Se$: C, 51.43; H, 5.40; N, 14.99. Found: C, 51.48; H, 5.52; N, 15.03.

1-(Azidomethyl)cyclopentene (14) and (azidomethylene)cyclopentane (15): IR (neat) 2100 cm^{-1}; ^1H NMR δ (14) 5.72-5.65 (m, 1 H), 3.9-3.78 (bs, 2 H), 2.5-2.3 (m, 4 H), 2.02-1.88 (m, 2 H); (15) 5.18-5.1 (m, 1 H), 2.5-2.3 (m, 8 H); ^{13}C NMR δ (14) 138.5, 129.4, 51.4, 33.4, 32.4, 23.5 (15) 138.5, 131.7, 32.9, 23.0; MS m/e (rel intensity) (14) 123 (M, 10), 95 (12), 94 (36), 81 (52), 68 (33), 67 (100), 55 (40), 41 (93); (15) 123 (M, 7), 91 (21), 94 (50), 81 (49), 68 (30), 67 (100), 55 (37), 41 (87). Anal. Calcd for $C_6H_9N_3$: C, 58.52; H, 7.37; N, 34.12. Found: C, 58.58; H, 7.46; N, 34.18.

1-(Azidomethyl)-2-[(phenylseleno)methyl]cyclopentane (19): oil; IR (neat) 2090 cm^{-1}; ^1H NMR δ 7.6-7.4 (m, 2 H), 7.3-7.1 (m, 3 H), 3.34 (dd, 1 H, J = 6.5 and 12.2 Hz), 3.18 (dd, 1 H, J = 7.7 and 12.2 Hz), 2.98 (dd, 1 H, J = 5.9 and 11.5 Hz), 2.76 (dd, 1 H, J = 9.0 and 11.5 Hz), 2.35-2.15 (m, 2 H), 2.0-1.3 (m, 6 H); ^{13}C NMR δ 132.5, 130.5, 128.9, 126.7, 52.0, 42.1, 42.0, 31.4, 29.0, 28.9, 22.5; MS m/e (rel intensity) 295 (1), 185 (34), 171 (13), 157 (45), 110 (38), 91 (37), 81 (100), 67 (27), 55 (22), 41 (57). Anal. Calcd for $C_{13}H_{15}N_3Se$: C, 53.43; H, 5.17; N, 14.38. Found: C, 53.51; H, 5.29; N, 14.45.

7-Azido-6-(phenylseleno)-1-heptene (20): oil, IR (neat) 2100 cm^{-1}; ^1H NMR δ 7.7-7.5 (m, 2 H), 7.3-7.1 (m, 3 H), 5.9-5.63 (m, 1 H), 5.1-4.9 (m, 2 H), 3.55 (dd, 1 H, J = 5.4 and 12.5 Hz), 3.38 (dd, 1 H, J = 7.5 and 12.5 Hz), 3.3-3.15 (m, 1 H), 2.3-1.5 (m, 6 H); ^{13}C NMR δ 138.0, 135.2, 133.2, 129.1, 127.9, 114.9, 55.9, 44.4, 33.2, 31.9, 26.7; MS m/e (rel intensity) 295 (5), 267 (4), 172 (10), 110 (77), 106 (31), 91 (42), 78 (81), 67 (64), 41 (100). Anal. Calcd for $C_{13}H_{17}N_3Se$: C, 53.06; H, 5.82; N, 14.28. Found: C, 52.97; H, 5.75; N, 14.25.

1,7-Diazido-2,6-bis(phenylseleno)heptane (21): oil; IR (neat) 2090 cm^{-1}; ^1H NMR δ 7.6-7.45 (m, 8 H), 7.35-7.15 (m, 12 H), 3.55 (dd, 2 H, J = 5.3 and 12.5 Hz), 3.54 (dd, 2 H, J = 5.4 and 12.5 Hz), 3.41 (dd, 2 H, J = 7.4 and 12.5 Hz), 3.38 (dd, 2 H, J = 7.5 and 12.5 Hz), 3.2-3.05 (m, 4 H), 1.9-1.4 (m, 12 H); ^{13}C NMR δ 135.3, 133.1, 129.1, 128.0, 55.8, 44.2, 44.0, 32.0, 31.9, 25.6, 25.5. Anal. Calcd for $C_{19}H_{22}N_6Se_2$: C, 46.35; H, 4.50; N, 17.07. Found: C, 46.41; H, 4.61; N, 17.11.

1-(Azidomethyl)-4-[2-(phenylseleno)propyl]cyclohexane (25): oil; IR (neat) 2090 cm^{-1}; ^1H NMR δ 7.7-7.6 (m, 2 H), 7.4-7.2 (m, 3 H), 5.7-5.65 (m, 1 H), 3.7-3.5 (m, 2 H), 2.4-1.2 (m, 12 H); ^{13}C NMR δ 138.3, 132.4, 128.4, 128.3, 127.7, 126.2, 57.0, 51.3, 44.0, 28.2, 27.7, 27.4, 26.5, 25.0; MS m/e (rel intensity) 177 (M^+ - PhSeH, 7), 158 (35), 150 (56), 135 (25), 108 (100), 106 (52), 91 (30), 78 (44), 67 (28), 41 (36). Anal. Calcd for $C_{16}H_{21}N_3Se$: C, 57.48; H, 6.33; N, 12.57. Found: C, 57.55; H, 6.46; N, 12.60.

1-(Azidomethyl)-4-(1-methylethenyl)cyclohexene (26): oil; IR (neat) 2090 cm^{-1}; ^1H NMR δ 5.8-5.7 (m, 1 H), 4.8-4.68 (m, 2 H), 3.72-3.58 (m, 2 H), 2.4-1.74 (m, 10 H): ^{13}C NMR δ 149.1, 132.2, 126.2, 108.9, 57.4, 40.7, 30.4, 27.3, 27.1, 20.7; MS m/e (rel intensity) 149 ($M^+ - N_2$, 14), 134 (37), 106 (33), 93 (44), 91 (60), 68 (100), 67 (87), 53 (46), 41 (63). Anal. Calcd for $C_{10}H_{15}N_3$: C, 67.76; H, 8.53; N, 23.71. Found: C, 67.71; H, 8.49; N, 23.69.

2-Azido-1-(phenylseleno)ethyl crotonate (34): oil; IR (neat) 2100 and 1730 cm^{-1}; ^1H NMR δ 7.6-7.5 (m, 2 H), 7.4-7.2 (m, 3 H), 7.06 (dq, 1 H, J = 6.8 and 15.5 Hz), 6.29 (dd, 1 H, J = 5.3 and 7.8 Hz), 5.88 (dq, 1 H, J = 1.7 and 15.5 Hz), 3.56-3.52 (m, 2 H), 1.91 (dd, 3 H, J = 1.7 and 6.8 Hz); ^{13}C NMR δ 164.4, 146.7, 136.2, 129.1, 128.8, 121.7, 72.3, 54.8, 18.0; MS m/e (rel intensity) 311 (1), 157 (7), 154 (8), 77 (9), 69 (100), 51 (6), 41 (15). Anal. Calcd for $C_{12}H_{13}N_3O_2Se$: C, 46.30; H, 4.21; N, 13.51. Found: C, 46.37; H, 4.30; N, 13.55.

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Registry No. 1, 116316-13-3; 2, 73501-69-6; 3, 136061-58-0; 4, 136061-59-1; 5, 136061-60-4; 6, 136061-61-5; 7, 136061-62-6; 8, 136061-63-7; 9 (isomer 1), 136061-64-8; 9 (isomer 2), 136061-70-6; *cis*-10, 136061-65-9; *trans*-10, 116316-04-2; 11, 116316-12-2; 12, 136061-66-0; 13, 136061-67-1; 14, 136061-68-2; 15, 136061-69-3; 16, 3070-53-9; *cis*-19, 136061-71-7; *trans*-19, 136061-79-5; 20, 136061-72-8; 21 (isomer 1), 136088-50-1; 21 (isomer 2), 136061-80-8; 22, 127-91-3; 25, 136061-73-9; 26, 136061-74-0; 27, 110-87-2; 28, 136061-75-1; 29, 136061-76-2; 30, 96-33-3; 31, 136061-77-3; 32, 16717-78-5; 33, 3234-54-6; 34, 136061-78-4; NaN_3, 26628-22-8; $(PhSe)_2$, 1666-13-3; styrene, 100-42-5; 1-octene, 111-66-0; allylbenzene, 300-57-2; 5-hexen-2-one, 109-49-9; methyl 3-butenoate, 3724-55-8; methyl 4-pentenoate, 818-57-5; methyl 5-hexenoate, 2396-80-7; methylenecyclopentane, 1528-30-9; (*E*)-4-octene, 14850-23-8; cyclohexene, 110-83-8.

Supplementary Material Available: Physical and spectral data of compounds 9, 10, 3, 5, 6, 7 (3 pages). Ordering information is given on any current masthead page.

Addition of Semidione Radicals to Arenediazonium Ions: Synthesis of 1,1-Diacyl-2-arylhydrazines

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The α-dicarbonyl compounds **1** are selectively reduced to semidione radicals **2** by aqueous Ti^{3+}, via inner-sphere electron transfer (ET). When an equimolar amount of an arenediazonium salt (**3**) is present, **2** adds to the nitrogen-nitrogen triple bond of **3** to afford the intermediate azo radical cation C, which, depending on the nature of the para substituent of the *N*-phenyl ring, undergoes rearrangement to a 1,1-diacyl-2-arylhydrazine (**4**) or preferentially reduction to a hydrazone (**5**). A mechanism that accounts for both the rearrangement and the substituent effects that are observed is proposed.

We recently showed[1] that the α-dicarbonyl compounds **1a,b,d** are reduced by aqueous titanium trichloride to the intermediate semidone radicals **2**. These stereoselectively add to the carbonyl group of aldehydes to afford α,β-dihydroxy ketones (Scheme I).

It was postulated that the addition proceeds via a radical-chelated Ti(IV) species (**2**). Chelation would restrict the number of possible transition states and would thereby lead to stereoselective addition.

We now report that, under similar experimental conditions, radicals **2a-d** add to the nitrogen-nitrogen triple bond of arenediazonium ions **3** to give, via the intermediate

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(2) Biacetyl (**1c**) undergoes reductive dimerization on treatment with Ti^{3+}. Clerici, A.; Porta, O. Unpublished results.

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