Group Transfer Addition Reactions of Methyl(phenylseleno)malononitrile to Alkenes

Dennis P. Curran,* Eugen Eichenberger, Maree Collis, Michael G. Roepel, and Gebhard Thoma†

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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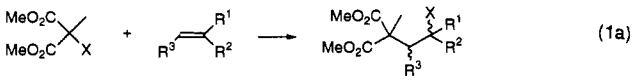
Abstract: Results of a detailed study of group transfer additions of methyl(phenylseleno)propanedinitrile (**4**) to a wide variety of alkenes are reported. For example, heating of **4** (60 °C) with 1-hexene and AIBN produces (2-(phenylseleno)-hexyl)methylpropanedinitrile in 97% yield. Reagent **4** adds in high yields to monosubstituted styrenes, enol ethers, enol acetates, enol sulfides, enamides, and enol imidazoles and carbazoles. Additions to many classes of 1,2-disubstituted alkenes also occur, and modest to good levels of 1,2-asymmetric induction are observed in the selenium transfer step. Oxygen- and sulfur-substituted alkenes produce anti products, and *N*-substituted alkenes produce syn products. The proposed mechanism involves radical addition followed by phenylselenium group transfer, and it is shown that radical additions to certain classes of disubstituted alkenes can be reversible. Additions to trisubstituted alkenes fail, probably because of this reversibility. Competition studies provide a relative reactivity scale of alkenes toward the electrophilic methylpropanedinitrile radical. Finally, a series of transformations serve to illustrate some synthetic possibilities for the products of these selenium transfer addition reactions.

Introduction

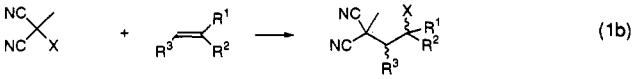
The atom transfer method has emerged as one of the methods of choice for conducting addition and cyclization reactions of electrophilic radicals, and many of the features and benefits of this method are now well recognized.[1] Several years ago, we introduced iodomalonic esters **1** as powerful reagents for use in iodine-transfer addition, cyclization, and annulation reactions (see eq 1a).[2] While the cyclization reactions of iodomalonic esters were exceptionally general, the addition (and annulation) reactions were limited by the nature of the alkene partner: most di- and trisubstituted alkenes were not reactive enough to sustain good chains. To solve this problem, we recently introduced iodomalononitriles **3**.[3] These reagents are quite unusual in that they propagate atom transfer chains even in the presence of molecular iodine.[3b,d] They also add to important classes of di- and trisubstituted alkenes (see eq 1b).



(1a)

1 X = I (ref. 2) works with mono- and 1,1-dialkyl- and phenyl-substituted alkenes fails with 1,2-di- and tri-substituted alkenes, enol ethers, enamines

2 X = SePh (ref. 7) works with alkenes, styrenes, enol ethers fails with 1,2-di- and tri-substituted alkenes



(1b)

3 X = I (ref. 3) works with mono-, di-, and trialkyl- and phenyl- substituted alkenes fails with enol ethers, enamines

4 X = SePh (this work) works with monosubstituted alkenes, styrenes, enol ethers, enamides fails with 1,2-di-, and tri-alkylsubstituted alkenes

A major limitation of both iodomalononitriles **3** and iodomalonic esters **1** concerned electron-rich alkenes like enol ethers, enol thioethers, and enamines. Despite the apparent favorable electronic pairing (electron-poor radical, electron-rich acceptor), attempted reactions of **1** and **3** with these classes of alkenes consistently gave disastrous results:[4] mixing of **1** or **3** with a heteroatom-substituted alkene **5** led only to disappearance of either or both reaction components with no apparent formation of adducts. We hypothesized that ionic reactions of these pairs of reagents might occur more rapidly than a radical chain. Iodomalonic esters and iodomalononitriles must be good sources of iodonium ions, and the precedented[5] ionic pathway shown in eq 2 could occur. Decomposition could plausibly take place at the stage of intermediate ions **6**. The products **7** of such reactions are not expected to be very stable either. We tried a few unsuccessful experiments to trap the supposed intermediates or products by adding other nucleophiles. Though it is still possible that successful ionic additions could be designed along the lines suggested by eq 2, we turned instead to solving the problems of the radical addition.

Because the phenylselenium group is less electropositive than iodine, phenylselenomalonic esters **2** and malononitriles **4** might be more reluctant to participate in the (hypothetical) ionic reactions in eq 2 yet might still participate in the radical reactions of eq 1. Radical additions of PhSe–X bonds across carbon–

† Current address: Central Research Laboratories, Ciba-Geigy, CH-4002, Basel, Switzerland.

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(1) Reviews: (a) Curran, D. P. In *Free Radicals in Synthesis and Biology;* Minisci, F., Ed; Nato ASI Series C; Kluwer: Dordrecht, 1989; Vol. 260, pp 27–36. (b) Curran, D. P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 4, pp 715–778, 779–832.

(2) (a) Curran, D. P.; Chen, M. H.; Spletzer, E.; Seong, C. M.; Chang, C. T. *J. Am. Chem. Soc.* **1989**, *111*, 8872. (b) Curran, D. P.; Chang, C. T. *J. Org. Chem.* **1989**, *54*, 3140. (c) Curran, D. P.; Bosch, E.; Kaplan, J.; Newcomb, M. *J. Org. Chem.* **1989**, *54*, 1826.

(3) (a) Curran, D. P.; Seong, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 9401. (b) Curran, D. P.; Seong, C. M. *Tetrahedron* **1992**, *48*, 2157. (c) Curran, D. P.; Seong, C. M. *Tetrahedron* **1992**, *48*, 2175. (d) Curran, D. P.; Thoma, G. *Tetrahedron Lett.* **1991**, *32*, 6307. (e) Curran, D. P.; Shu, M. *Bull. Soc. Chim. Fr.* **1993**, *130*, 314.

(4) (a) Chang, C.-T. Ph.D. Thesis, University of Pittsburgh, 1989. (b) Seong, C.-M. Ph.D. Thesis, University of Pittsburgh, 1991. (c) Thoma, G. Unpublished observations.

(5) Examples of ionic reactions of malononitriles: (a) Curran, D. P.; Morgan, T. M.; Schwartz, C. E.; Snider, B. B.; Dombroski, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 6607. (b) Beckwith, A. L. J.; Tozer, M. J. *Tetrahedron Lett.* **1992**, *33*, 4975. (c) Kitagawa, O.; Inoue, T.; Taguchi, T. *Tetrahedron Lett.* **1992**, *33*, 2167. (d) Kitagawa, O.; Inoue, T.; Hirano, K.; Taguchi, T. *J. Org. Chem.* **1993**, *58*, 3106.

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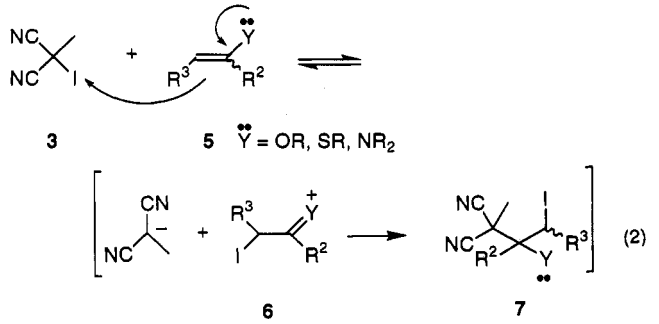


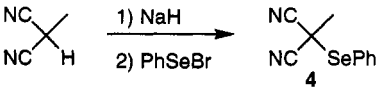
carbon multiple bonds were well-known,[6] so it was clear that carbon-centered radicals could abstract selenophenyl groups from sufficiently reactive donors. Just prior to the initiation of our work, Byers and co-workers reported several addition and cyclization reactions of selenomalonic esters.[7] These were the first examples of additions of PhSe–C bonds across carbon–carbon multiple bonds.

On the basis of the expanded scope of halomalononitrile radical additions relative to halomalonic ester additions, we undertook a detailed study of the scope, limitations, mechanism, stereochemistry, and preparative utility of selenium transfer addition and cyclization reactions of selenomalononitriles. Some of our early observations have appeared in a preliminary communication,[8] and we now report the full details of our study. Selenomalononitrile reagents are valuable supplements and complements to their relatives in eq 1. More generally, recent work from a number of groups[9] is now showing that phenylchalcogen (SPh, SePh, TePh) transfer reactions parallel halogen transfer reactions in their scope, yet can offer advantages of precursor and product stability while at the same time opening new avenues for transformations of the products.

Additions to Monosubstituted Alkenes

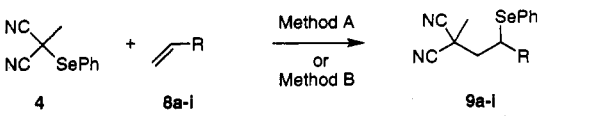
Methyl(phenylseleno)malononitrile (**4**) was readily prepared by deprotonation of methylmalononitrile[10] with sodium hydride followed by addition of benzeneselenenyl bromide (eq 3). Phenylselenide **4** was isolated as a yellow solid (mp 71–72 °C) in 77% yield after standard workup and flash chromatography. We routinely stored this solid in the freezer, though experience taught us that **4** is a stable compound that can be weighed and handled in air and light like any standard organic solid.

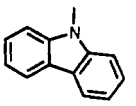
We attempted to add **4** to a number of terminal alkenes **8** under several different conditions. Though iodide **3** can be induced to add to alkenes simply by warming at 60 °C, heating solutions of **4** and alkenes up to 120 °C did not induce reaction; both partners were recovered unchanged. Attempted initiation with



triethylborane/O_2 was also ineffective.[11] Simple irradiation of a mixture of an alkene and **4** in benzene at 60 °C with a sunlamp led to rapid (10 min) consumption of **4** but variable yields of adducts **9**, as shown in Table 1, method A. Addition of **4** to ethyl vinyl ether (entry d) proceeded smoothly to give **9d** in 97% yield. However, photolytic addition to 1-hexene gave **9a** in only 20% yield alongside large amounts of 2,2,3,3-tetracyanobutane (the dimer of the methylmalononitrile radical). Photolytic addition to styrene (entry c) gave **9c** in only 30% yield alongside large amounts of insoluble (probably polymeric) material. These results suggest that photolytic initiation is too efficient and exceeds the rate of a chain propagation step.

Table 1. Additions of 4 to Monosubstituted Alkenes



entry	R	method[a]	time	% yield
a	C_4H_9	A	10 min	20
		B	40 h	97
b	CO_2Me	B	120 h	*b*
c	Ph	A	10 min	30
		B	120 h	84
d	OEt	A	10 min	97
		B	2 h	99
e	OAc	B	24 h	97
f	SPh	B	2 h	99
g		B	120 h	91
h		B	5 h	84
i		B	16 h	97

[a] Method A: sunlamp irradiation, C_6H_6, 60 °C. Method B: AIBN, $CHCl_3$, 60 °C. [b] No product isolated.

By far the best conditions for addition involved thermolytic initiation with AIBN. Warming of a chloroform solution of **4** (0.1 M), an alkene (2 equiv), and AIBN (0.05 equiv) resulted in smooth conversion to adducts **9a–i**, as detailed in Table 1, method B. Selenomalononitrile **4** adds well to good partners for iodomalononitrile **3** like 1-hexene and styrene (entries a and c), but it also adds to a broad range of alkenes that **3** does not. These include enol ethers (entry d), enol acetates (entry e), enol sulfides (entry f), enamides (entry h), vinylimidazoles (entry g), and vinylcarbazoles (entry i). Given these favorable results, we believe that **4** will add to many more classes of vinyl heteroatom substrates. So far, we have identified two limitations for monosubstituted alkenes. First, phenylselenide **4** will not add to enamines; instead only decomposition occurs. However, the additions succeed if electron-withdrawing groups are present on nitrogen (entries g–i). Second, compound **4** will also not add to electron-poor alkenes like methyl acrylate (entry b); in such cases, no reaction occurs. Iodide **3** will add to alkenes like methyl acrylate and acrylonitrile with reasonable efficiency (65–80%).

The approximate reaction times for complete addition vary widely as a function of substrate. The fastest reactions (with

(6) Examples and leading references: (a) Back, T. G.; Krishna, M. V. *J. Org. Chem.* **1988**, *53*, 2533. (b) Back, T. G.; Krishna, M. V.; Muralidharan, K. R. *Tetrahedron Lett.* **1987**, *28*, 1737. (c) Toru, T.; Seko, T.; Maekawa, E.; Ueno, Y. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1927. (d) Ogawa, A.; Yokayama, H.; Yokayama, K.; Masawaki, T.; Kambe, N.; Sonoda, N. *J. Org. Chem.* **1991**, *56*, 5721.

(7) (a) Byers, J. H.; Gleason, T. G.; Knight, K. S. *J. Chem. Soc., Chem. Commun.* **1991**, 354. (b) Byers, J. H.; Lane, G. C. *Tetrahedron Lett.* **1990**, *31*, 5697. (c) See also: Kropp, P. J.; Fryxell, G. E.; Tubergen, M. W.; Hager, M. W.; Harris, G. D., Jr.; McDermott, T. P., Jr.; Tornero-Velez, R. *J. Am. Chem. Soc.* **1991**, *113*, 7300.

(8) Curran, D. P.; Thoma, G. *J. Am. Chem. Soc.* **1992**, *114*, 4436.

(9) (a) These biomolecular chalcogen transfer reactions follow in the steps of well-known intramolecular transfers. See: Kampmeier, J. A.; Jordan, R. B.; Liu, M. S.; Yamanaka, H.; Bishop, D. J. *Organic Free Radicals*; Pryor, W. A., Ed., ACS Symposium Series C; American Chemical Society: Washington, DC, 1978; p 16. (b) Byers, J. H.; Harper, B. C. *Tetrahedron Lett.* **1992**, *33*, 6953. (c) Chen, C.; Crich, D.; Papadatos, A. *J. Am. Chem. Soc.* **1992**, *114*, 8313. (d) Han, L. B.; Ishihara, K. I.; Kambe, N.; Ogawa, A.; Ryu, I. H.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 7591. (e) Chen, C.; Crich, D. *Tetrahedron Lett.* **1993**, *34*, 1545. (f) Byers, J. H.; Lane, G. C. *J. Org. Chem.* **1993**, *58*, 3355. (g) Curran, D. P.; Martin-Esker, A. A.; Ko, S.-B; Newcomb, M. *J. Org. Chem.* **1993**, *58*, 4691. (h) Renaud, P.; Vionnet, J. P. *J. Org. Chem.* **1993**, *58*, 5895. (i) Vionnet, J. P.; Schenk, K.; Renaud, P. *Helv. Chim. Acta* **1993**, *76*, 2490. (j) Pandey, G.; Rao, K. S. S. P.; Sekhar, B. B. V. S. *J. Chem. Soc., Chem. Commun.* **1993**, 1636.

(10) Hosmane, R. S.; Bakthavachalam, V.; Leonard, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 235.

(11) Miura, K.; Ichinose, Y.; Nozaki, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1989**, *52*, 143.

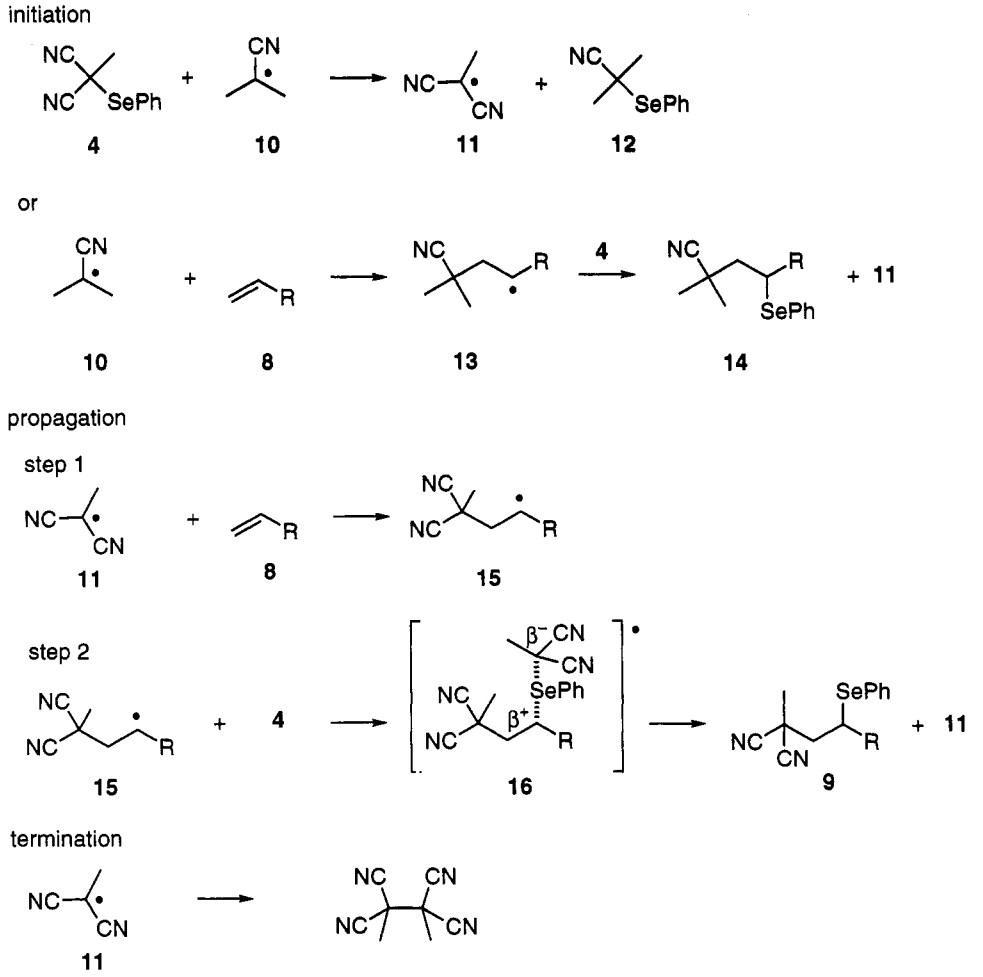


Figure 1. Mechanism of phenylselenium group transfer addition.

substrates like enol ethers, enol thioethers, and enamides, entries d, e, h) are complete in several hours, while the slowest reactions (with substrates like styrene and vinyl carbazole, entries c, g) take up to 5 days. Despite the long reaction times, all the reactions are clean and high-yielding.

Mechanism

The addition of (phenylseleno)malononitriles to alkenes occurs by a radical chain mechanism. Evidence in support of this conclusion includes the following: (1) reactions do not occur thermally, but must be initiated with AIBN or by photolysis; (2) reaction rates are retarded by radical inhibitors; (3) the regiochemistry in all addition reactions is consistent with a radical, not an ionic, addition (compare the ionic pathway in eq 2 with the results in Table 1); (4) additions to disubstituted alkenes (see examples in Table 2) are stereoselective, not stereospecific (in other words, isomeric *E* and *Z* alkenes give the same products in the same ratios); (5) when comparable, stereo- and regiochemical results in phenylselenium transfer additions of **4** always parallel results of iodine transfer additions of **3** (which are known to proceed through radical chains[3]).

The proposed mechanism for this transformation is summarized in Figure 1. Initiation by AIBN could involve either phenylselenium abstraction from **4** by the isobutyronitrile radical **10** or addition of radical **10** to an alkene to give **13** followed by phenylselenium transfer to give **14**. In either case, malononitrile radical **11** is produced. Propagation steps consist of radical addition (step 1) and phenylselenium group transfer (step 2). Additions of malononitrile radicals to electron-rich alkenes are known,[12] so step 1 is well precedented. The mechanistic evidence cited above strongly supports the viability of phenylselenium transfer (step 2). Chain termination occurs mostly through dimerization of the methylmalononitrile radical (**11**). Large amounts of the termination product are formed under conditions of very efficient initiation (photolysis) or with poor substrates for addition.[13]

For terminal alkenes, a comparison of reaction times with relative reactivities of alkenes shows no correlation. For example, styrene is marginally more reactive than ethyl vinyl ether toward the methylmalononitrile radical (see competition experiments below), yet the reaction with ethyl vinyl ether takes 2 h and that with styrene takes 5 days (compare entries c and d in Table 1). Assuming that the rate of the initiation step is relatively constant, this suggests that the selenium transfer step is rate limiting. The rate of the phenylselenium transfer reaction is probably determined by a balance between radical stabilizing effects and polar effects. It is well-known that radical stabilizing groups strongly effect the rates of atom and group transfer reactions,[14] and many atom/group transfer chains are driven by a highly exothermic (hence rapid) transfer step. Radical stabilizing groups R on the alkene **8** may increase the rate of the radical addition step, but

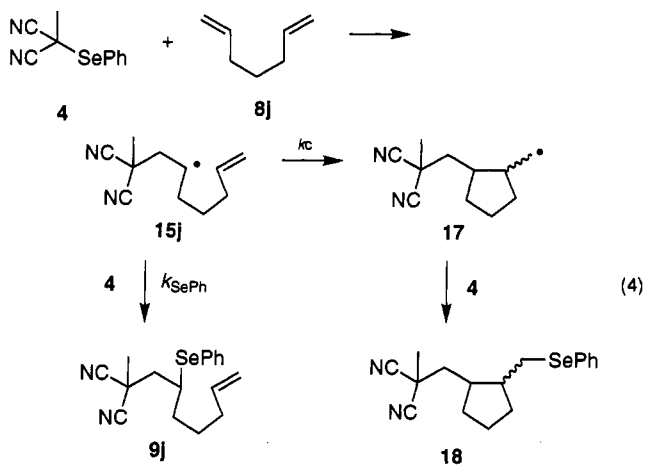
(12) (a) Riemenschneider, K.; Bartels, H. M.; Dornow, R.; Dreschel-Grau, E.; Eichel, W.; Luthe, H.; Matter, Y. M.; Michaelis, W.; Boldt, P. *J. Org. Chem.* **1987**, *52*, 205. (b) Boldt, P.; Schulz, L.; Klinsmann, U.; Köster, H.; Thielecke, W. *Tetrahedron* **1970**, *26*, 3591. (c) Boldt, P.; Schulz, L.; Etzemüller, J. *Chem. Ber.* **1967**, *100*, 1281. (d) Boldt, P.; Schulz, L. *Tetrahedron Lett.* **1967**, 4351.

(13) This could occur under two types of circumstances: (1) if the forward addition rate is very low (hindered alkenes) or (2) if the reverse addition competes with selenium transfer.

(14) (a) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangement in the Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, p 161. (b) Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 1, p 133.

the same radical stabilizing groups on adduct radical **15** will lower the enthalpy of phenylselenium transfer and hence reduce its rate. Indeed with good radical stabilizing groups R like Ph, OEt, or NR_2, the phenylselenium transfer step may begin to approach thermoneutrality. In the absence of favorable polar effects, we can predict that thermoneutral phenylselenium transfer reactions will not be sufficiently rapid to propagate a chain.[15] We suggest that these chains can be propagated with stabilized radicals because of a favorable polar effect that accelerates (both forward and reverse) phenylselenium group transfer. This polar effect is illustrated in step 2, structure **16**, and there is precedent for this effect in halogen transfer reactions.[16] It is not entirely clear whether **16** is an intermediate or a transition state. Barton has implied that phenyltellurium transfer reactions are stepwise.[17] But *ab initio* calculations[18] suggest that selenium and sulfur transfer reactions are concerted, and our recent measurements[9g] of substituent effects on rate provide support for **16** as a transition state.

Further evidence for the radical chain mechanism and a first estimate for a rate constant of a phenylselenium transfer reaction came from the addition of **1** to heptadiene (**8j**) shown in eq 4.



(4)

This addition provided mixtures of direct addition product **9j** and tandem addition/cyclization[19] product **18**. As predicted by the standard mechanism shown in eq 4, we observed the anticipated dependence of the **9j**/**18** ratio on the concentration of the starting malononitrile **4**. By making some reasonable assumptions about the rate constant for cyclization of **15j**,[20] we can estimate a rough rate constant for the abstraction of a phenylselenium group from **4** by secondary-alkyl radical **15j**: $k_{SePh} \approx 3 \times 10^6\ M^{-1}\ s^{-1}$. Very recently, we have measured the rate constant for the reaction the primary-octyl radical with **4**: $k_{SePh} = 8 \times 10^6\ M^{-1}\ s^{-1}$.[9g]

(15) Recent measurements have shown that rate constants for bromine transfer from RBr and phenylselenium transfer from RSePh are comparable (ref 9f). Thermoneutral bromine transfer reactions cannot generally be used to propagate chains. See: Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206.

(16) Giese, B.; Hartung, J. *Chem. Ber.* **1992**, *125*, 1777.

(17) (a) Barton, D. H. R.; Ozbalik, N.; Sarma, J. C. *Tetrahedron Lett.* **1988**, *29*, 6581. (b) Barton, D. H. R.; Dalko, P. I.; Géro, S. D. *Tetrahedron Lett.* **1991**, *32*, 4713. (c) Barton, D. H. R.; Camara, J.; Cheng, X.; Gero, S. D.; Jaszberenyi, J. C.; Quiclet-Sire, B. *Tetrahedron* **1992**, *48*, 9261.

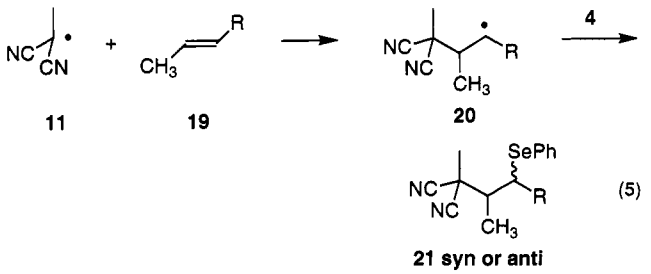
(18) (a) Lyons, J. E.; Schiesser, C. H. *J. Organomet. Chem.* **1992**, *437*, 165. (b) Schiesser, C. H.; Sutej, K. *J. Chem. Soc., Chem. Commun.* **1992**, 57. (c) Schiesser, C. H.; Sutej, K. *Tetrahedron Lett.* **1992**, *33*, 5137.

(19) Recent examples of such tandem addition/cyclizations: (a) Miura, K.; Oshima, K.; Utimoto, K. *Chem. Lett.* **1992**, 2477. (b) De Riggi, I.; Gastaldi, S.; Surzur, J. M.; Bertrand, M. P.; Virgili, A. *J. Org. Chem.* **1992**, *57*, 6118. (c) Brumwell, J. E.; Simpkins, N. S.; Terrett, N. K. *Tetrahedron Lett.* **1993**, *34*, 1219. (d) Naim, A.; Mills, G.; Shevlin, P. B. *Tetrahedron Lett.* **1992**, *33*, 6779. (e) Chuang, C. P.; Ngoi, T. H. J. *J. Chin. Chem. Soc.* **1992**, *39*, 439.

(20) We estimate that k_c for **15j** is approximately equal to that of the parent hexenyl radical at 60 °C, $k_c = 7 \times 10^5\ s^{-1}$. At [0.2 M] starting concentration of **4**, the observed ratio **9j**/**18** was 0.25. The rate constant was then estimated by using standard second-order kinetic equations.

Additions to 1,2-Disubstituted Alkenes

The development of reagent **4** was a crucial advance in the search for a reagent that would add to 1,2-disubstituted alkenes in good yields by a radical mechanism. Addition reactions of **4** to 1,2-disubstituted alkenes would constitute a facile method to survey substrate-controlled 1,2-asymmetric induction in a variety of systems.[21-23] The concept is outlined in eq 5. Addition of radical **11** to a disubstituted alkene **19** proceeds via the intermediacy of chiral radical **20** and can yield syn and anti products **21** through diastereomeric selenium transfer transition states. This particular addition reaction is valuable because the chiral radical **20** bears an adjacent stereocenter with a small (H), a medium (CH_3), and a large (malononitrile) group. Thus, selective group transfers based on steric effects can be studied. Furthermore, the nature of the radical-bearing substituent R could be changed, providing new information about radical substituent effects on 1,2-asymmetric induction. Though asymmetric selenium transfer reactions may have limited synthetic potential, these reactions are models for more useful C–C and C–H bond forming reactions.



(5)

The results of the selenium transfer additions of **4** to disubstituted alkenes are summarized in Table 2. All reactions were conducted by method B (0.05 equiv of AIBN, 60 °C), and isolated yields were determined after flash chromatography. These reactions were very slow, taking 2–10 days, but were relatively clean and high-yielding. In most cases, the syn and anti isomers were separable; configurational assignments are discussed below. The brief survey of substrates suggests that phenylselenium transfer reagents like **4** can be used preparatively for additions to many classes of cyclic and acyclic alkenes.

The addition of **4** to cyclopentene (entry a) was highly trans selective, while addition to dihydropyran (entry b) exhibited a modest trans selectivity.[24] As expected from iodine and hydrogen transfer additions,[3d] addition to β-methylstyrene (entry c) occurred with moderate syn selectivity through the intermediacy of a benzyl

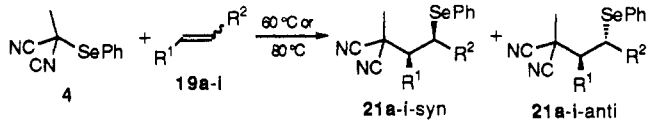
(21) Review: Porter, N. A.; Giese, B.; Curran, D. P. *Acc. Chem. Res.* **1991**, *24*, 296.

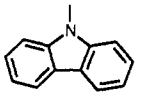
(22) Leading references to π-conjugated radicals: (a) Hart, D. J.; Huang, H.-C.; Krishnamurthy, R.; Schwartz, T. *J. Am. Chem. Soc.* **1989**, *111*, 7507. (b) Hart, D. J.; Krishnamurthy, R. *J. Org. Chem.* **1992**, *57*, 4457. (c) Erdmann, P.; Schäfer, J.; Springer, R.; Zeitz, H.-G.; Giese, B. *Helv. Chim. Acta* **1992**, *75*, 638. (d) Durkin, K.; Liotta, D.; Rancourt, J.; Lavallée, J.-F.; Boisvert, L.; Guindon, Y. *J. Am. Chem. Soc.* **1992**, *114*, 4912. (e) Curran, D. P.; Abraham, A. C. *Tetrahedron* **1993**, *49*, 4821. (f) Curran, D. P.; Ramamoorthy, P. S. *Tetrahedron* **1993**, *49*, 4841.

(23) Heteroatom-substituted radicals, oxygen: (a) Quintard, J. P.; Pereyre, M. *J. Organomet. Chem.* **1974**, *82*, 103. (b) Giese, B.; Damm, W.; Dickhaut, J.; Wetterich, F.; Sun, S.; Curran, D. P. *Tetrahedron Lett.* **1991**, *32*, 6097. (c) Giese, B.; Carboni, B.; Gobel, T.; Muhn, R.; Wetterich, F. *Tetrahedron Lett.* **1992**, *33*, 2673. (d) Giese, B.; Damm, W.; Roth, M.; Zehender, M. *Synlett* **1992**, 441. (e) Damm, W.; Dickhaut, J.; Wetterich, F.; Giese, B. *Tetrahedron Lett.* **1993**, *34*, 431. (f) Eksterowicz, J. E.; Houk, K. N. *Tetrahedron Lett.* **1993**, *34*, 427. Nitrogen: (g) Renaud, P.; Bjõrup, P.; Carrupt, P.-A.; Schenk, K.; Schubert, S. *Synlett* **1992**, 211. (h) Schubert, S.; Renaud, P.; Carrupt, P. A.; Schenk, K. *Helv. Chim. Acta* **1993**, *76*, 2473. (i) Curran, D. P.; Sun, S. N. *Tetrahedron Lett.* **1993**, *34*, 6181. Phosphine oxide: (j) Brandi, A.; Cicchi, S.; Goti, A.; Pietrusiewicz, K. M. *Tetrahedron Lett.* **1991**, *32*, 3265. Sulfoxide: (k) Snider, B. B.; Wan, B. Y.-F.; Buckman, B. O.; Foxmann, B. M. *J. Org. Chem.* **1991**, *56*, 328. (l) Beckwith, A. L. J.; Hersperger, R.; White, J. M. *J. Chem. Soc., Chem. Commun.* **1991**, 1151. Halogen: (m) Solladié-Cavallo, A.; Quazzotti, S.; Fischer, J.; DeCian, A. *J. Org. Chem.* **1992**, *57*, 174.

(24) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969.

Table 2. Additions of 4 to Disubstituted Alkenes



entry	R^1	R^2	equiv of **19**	time (h)/ temp (°C)	yield	**21**-syn/anti (cis/trans)
a	$-CH_2-CH_2-CH_2-$		10	120/60	55	(0/100)
b	$-O-CH_2-CH_2-CH_2-$		3	120/60	78	(30/70)
c	Me	Ph	2	240/60	80	80/20
d	Me	*i*-Pr	10	120/60		
e	Me	OEt	2	70/60	92	25/75
				12/80	95	28/72
f	Me	OPh	5	48/60	90	25/75
				30/80	93	25/75
g	Me	SPh	3	40/60	73	10/90
h	Me		3	120/60	75	71/29
i	Me		2	120/60	70	90/10
				24/80	75	88/12

radical. Reagent **4** did not react with *cis*-4-methyl-2-butene (entry d); however, subsequent iodine transfer additions to this alkene occurred with syn selectivity.[8] Additions to enol ethers occurred with modest anti selectivity through the intermediacy of α-oxy radicals (entries e, f), while the addition to an enol sulfide occurred with improved anti selectivity through an α-thio radical (entry g). Additions to vinylpyrrolidone and vinylcarbazole (entries h, i) occurred with moderate to good syn selectivity through α-nitrogen-substituted radicals. The transformations with nitrogen-[23g,h] and thio-substituted radicals were the first examples of 1,2-asymmetric induction in these classes. Better selectivities might be observed at lower temperatures, but unfortunately these chains did not propagate well below 60 °C. We conducted a few additions in benzene at 80 °C, and these more rapid reactions exhibited only marginally lower selectivities (entries e, f, i).

A series of control experiments supported the notion that the selenium transfer step is kinetically controlled. Most reactions were followed by ^1H NMR spectroscopy, and syn/anti ratios always remained constant. Subjection of several pure isomers to the reaction conditions also showed no isomerizations. Finally, there are close parallels between (irreversible) hydrogen transfer reactions and selenomalononitrile reactions (see below).

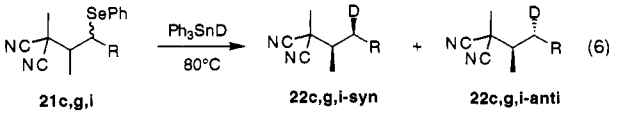
Substrate-controlled 1,2-asymmetric induction is now a topical theme of radical chemistry, and discussions of stereoselectivity for the transformations in Table 2 can be found in our work and that of others.[8,9h,21-23] In general, the results in Table 2 are consistent with emerging models. Nitrogen-substituted and π-conjugated radicals give syn products, as predicted by an A-strain model, and oxygen- and sulfur-substituted radicals give anti products, as predicted by a Felkin–Anh model. It is not clear why the selectivity with sulfur is better than that with oxygen (compare entries e and f with g).

Configurational Assignments

Conducting these radical additions and determining product ratios proved to be easy; it was the assignment of relative configurations of the products that was challenging. All of the adducts in Table 2 are new compounds, and many have no close analogs for which relative configurations are known. The difficulties are especially acute for adducts **21g**, whose syn and anti configurations differ only by a nuclear substitution of sulfur or selenium.

Assignment of the trans stereochemistry to **21a** was done by analogy to a large body of literature,[24] while magnitudes of vicinal coupling constants secured the structures of **21b**. Adduct **21c** was assigned by comparison of results and spectroscopic data with the related iodine and deuterium adducts.[3d] We assigned configurations to the other products by a combination of methods. Configurations of the enol ether adducts were assigned by using MM2 calculations[25] to interpret results of ^1H NMR experiments. MM2 calculations suggest that both syn and anti adducts **21e** favor conformations in which the phenylseleno and malononitrile groups are anti; conformations with these groups gauche are calculated to be at least 2 kcal/mol higher in energy. Assignments can now be made by using ^1H NMR data, as summarized in Figure 2. The anti isomer exhibits a small coupling constant J_{ab} and no observable NOE between H_b and the methyl group. The syn isomer **21e** exhibits a large J_{ab} and a large NOE between H_b and the methyl group.

Assignments in the nitrogen and sulfur series required other means because ^1H NMR data were ambiguous and MM2 calculations did not suggest that a single highly populated minimum was likely. Evidence for stereochemistry in these examples comes from subsequent reductions of the products. Treatment of a series of products with tributyltin deuteride under standard conditions provided mixtures of deuterated products (eq 6). The configurational assignments of products **22c**, **22g**, and **22i** are readily made with the aid of vicinal coupling constants. MM2 calculations suggest that all products **22** exist predominantly in conformations with R and the malononitrile group anti (Figure 2). Deuterated products with large vicinal proton–proton coupling constants J_{ab} are anti isomers, and those with small J_{ac} are syn isomers. Combined with earlier observations,[3d,23b] these results establish a parallel between direction and level of selectivity in the hydrogen, iodine, and phenylselenium transfer reactions of benzyl radicals and in the hydrogen and phenylselenium transfer reactions of α-oxy radicals. This parallel extends to nitrogen-[23g,h] and thio-substituted radicals as well, and we assign configurations to **21g–i** accordingly.



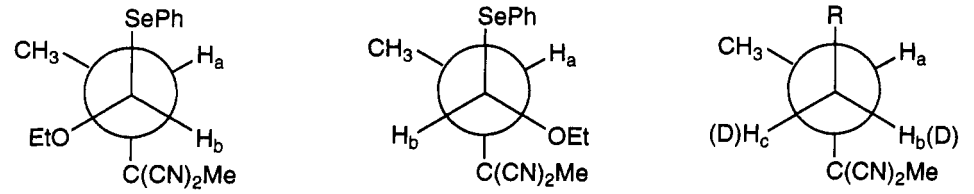
Precursor	Ratio **22**-syn/**22**-anti	R
21c	80/20	Ph
21g	17/83	SPh
21i	85/15	carbazole

There is no independent evidence that this parallel extends to sulfur-substituted radicals, but we have learned that the extension to nitrogen radicals is valid. Circumstantial support came from the elimination reactions of the selenoxides derived from **22h** (see below), and confirmation came from crystallography; the crystal structure of the minor isomer *anti*-**22h** was solved, and full details of this structure are provided in the supplementary material.

Reversible Addition Reactions

Additions to 1,2-disubstituted alkenes generate chiral disubstituted radicals. With the hope of extending the studies on 1,2-asymmetric induction to chiral trisubstituted radicals, we attempted addition reactions to the series of trisubstituted alkenes **23a–d**, shown in Figure 3. Unfortunately, attempted additions of **4** to **23** were uniformly unsuccessful, and no evidence was obtained for selenium transfer adducts in any case. In reactions with alkenes **23b–d** we observed only gradual decomposition of **4**.

(25) Conducted by using the MM2 force field in version 3.0 of the CAChe workstation.

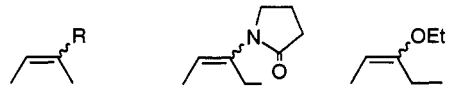


21e-anti J_{ab} = 2 Hz
no noe between H_b and CH_3

21e-syn J_{ab} = 9 Hz
large noe between H_b and CH_3

22 J_{ab} = 2-4 Hz
J_{ac} = 9-12 Hz

Figure 2.

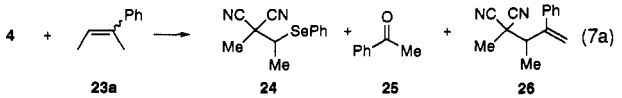


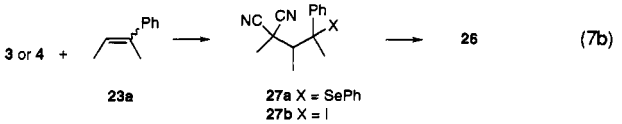
23a R = Ph
23b R = SPh

23c **23d**

Figure 3.

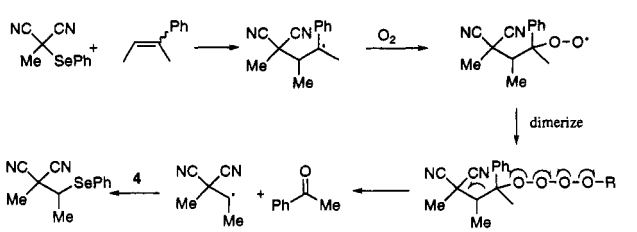
With styrene **23a**, we observed the slow formation of three products over several days, provided that AIBN was added daily (eq 7a). The two major products, obtained in about equal amounts (18% isolated), proved to be phenylselenide **24** and acetophenone (**25**). We assigned the structure of the minor product as substituted styrene **26** (13% isolated). The minor product **26** probably arises from successful selenium transfer addition, followed by ionic elimination of selenophenol from the intermediate adduct **27**. Evidence for this comes from the reaction of iodomalononitrile **3** with **23a**, which provides **26** as the major product in a slow reaction (eq 7b). The two major products from the addition of **4** to **23a** are apparently derived from reaction of intermediate radicals with O_2.[26] Evidence that the source of O_2 was the daily opening of the reaction system to add AIBN came when we conducted a rigorously degassed reaction in a sealed tube; after 24 h of heating, we could not detect the formation of any products in this reaction.

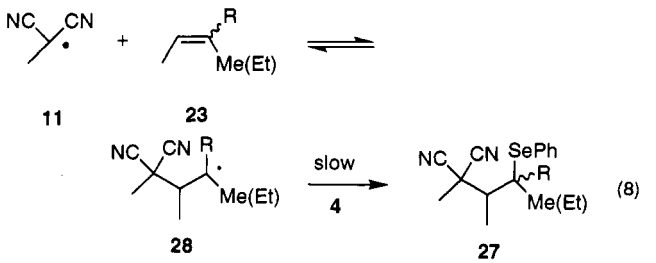




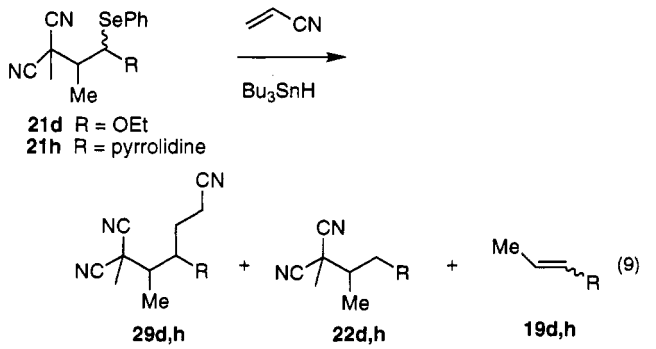
In relative rate studies with the parent malononitrile radical, Boldt and co-workers observed that trialkyl-substituted alkenes were often of similar reactivity to related dialkyl-substituted alkenes in direct competition experiments.[12a] This suggests that the failure of **4** to propagate chains with trisubstituted alkenes **23** is not due only to a slow addition step. Its seems likely that the addition of radical **11** to **23** occurs (eq 8), but that fragmentation of adduct **28** back to **11** and **23** is more rapid than phenylselenium transfer. In such a scenario, a chain may not propagate even though the addition reaction succeeds.

(26) We suggest below a speculative mechanism for the formation of **24** and **25**.





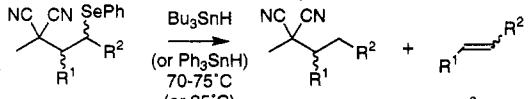
In principle, phenylselenium transfer adducts like those in Table 2 are radical precursors that can be used to regenerate chiral radicals for subsequent asymmetric reactions. This principle was demonstrated in the tin deuteride reductions of eq 6. In attempting to extend this idea to carbon–carbon bond forming reactions, we obtained instead more substantive evidence for fragmentation reactions of adducts like **27**. Attempts to reductively add several heteroatom-substituted products **21** to methyl acrylate or acrylonitrile by standard procedures provided low yields of adducts **29** along with directly reduced product **22** and alkene **19** (eq 9).



The unexpected observation of alkenes **19** as products prompted the study of the transformation of adducts **9** and **21** to **8** and **19** in more detail. Table 3 shows the results of reduction of several adducts **9** and **21** with tributyl- or triphenyltin hydride under a standard set of conditions (0.2 M **9** or **21**, 1.1 equiv of R_3SnH, 75 °C, C_6D_6). Alkenes **8** or **19** and reduced products **30** or **22** were formed in ratios that depended on the reaction conditions and the substituents of **9**/**21**. Several trends are apparent from the data in Table 3. The formation of significant amounts of alkenes **19** (entries 1–4) occurs only from adducts **21** of disubstituted ($R^1 \neq H$) enol ethers or enamines (R^2 = 2-pyrrolidone, carbazole, or OEt). Holding the substrate **21e** constant (entries 4–6), the yield of alkene decreases with increasing hydrogen donor ability of the tin hydride and decreases with decreasing temperature. Phenyl- and alkyl-substituted adducts with $R^1 = CH_3$ (**21c,j**) and adducts with $R^1 = H$ (**9d,h**) are not prone to formation of alkenes; instead these substrates give predominately or exclusively reduced products **30** or **22** (entries 7–10).

These results are consistent with the β-fragmentation mechanism shown in eq 10.[27] β-Fragmentations of alkyl radicals to

Table 3. Reduction of Adducts **9** and **21** with Bu_3SnH or Ph_3SnH

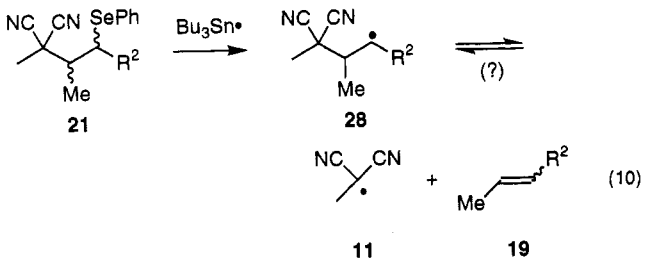


9 R^1 = H, **21** R^1 = Me — **30** R^1 = H, **22** R^1 = Me — **8** R^2 = H, **19** R^1 = Me

entry	precursor	R^1	R^2	reduced[a]		alkene (E/Z)[a]	
1	**21h**	CH_3	2-pyrrolidone	**22h**	20%	**19h**	80% (*E* only)
2	**21h** (Ph_3SnH)	CH_3	2-pyrrolidone	**22h**	70%	**19h**	30% (*E* only)
3	**21i**	CH_3	carbazole	**22i**	70%	**19i**	30% (*E* only)
4	**21e**	CH_3	OEt	**22e**	65%	**19e**	35% (45/55)
5	**21e** (Ph_3SnH)	CH_3	OEt	**22e**	90%	**19e**	10% (47/53)
6	**21e** (25 °C)	CH_3	OEt	**22e**	80%	**19e**	20% (40/60)
7	**21c**	CH_3	Ph	**22d**	>95%	**19d**	trace
8	**21**[b]	CH_3	*t*-Bu	**22j**	>95%	**19j**	ND[c]
9	**9d**	H	OEt	**30d**	>95%	**8d**	ND
10	**9h**	H	2-pyrrolidone	**30h**	>95%	**8h**	ND

[a] Isolated yields were not obtained, but ^{1}H NMR spectra suggest that all reactions are clean and high-yielding. Products were compared with authentic samples. [b] The corresponding iodide precursor was used; see ref 3d. [c] ND = not detected.

form C=C bonds are well-known,[28] but generally occur at high temperatures (>300 °C). However, substituent effects can reduce these temperatures significantly.[28c] The ease of the β-fragmentation of **28** is due in part to thermodynamic effects (regeneration of a stable malononitrile radical **11** and a conjugated alkene), but kinetic effects are clearly important. Branching (R^1 = Me) accelerates fragmentation, and the ease of fragmentation is not inversely related to the ability of R^2 to stabilize the radical **28**. Instead, the same electron-donating groups (NR_2, OR) that provide favorable polar effects to accelerate the addition of the electrophilic malononitrile radical to an alkene also accelerate its elimination from the adduct. Since β-fragmentation is the microscopic reverse of radical addition, it is not surprising that similar polar effects operate. Polar effects have also been identified in high-temperature β-fragmentation reactions of nucleophilic radicals.[28a,b]

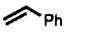
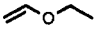
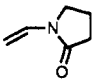
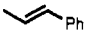
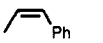
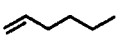
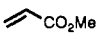
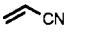


These results clearly illustrate that there are potential problems with addition reactions of malononitrile radical **11** or with subsequent reactions of an adduct radical **28** whenever the β-fragmentation reaction of **28** is faster than its trapping.

Relative Reactivities

To gain a better understanding of substituent effects on malononitrile radical additions, we conducted a series of competition experiments. Table 4 summarizes the relative reactivities of a number of representative alkenes toward the methylmalononitrile radical. These reactivities are given relative to 1-hexene, which arbitrarily assigned a reactivity of 1. The data considerably expand those of Boldt,[12a] who measured the relative reactivities of a number of alkyl-substituted alkenes to the parent malononitrile radical. The ratios were determined by standard competition experiments under pseudo-first-order conditions. A large excess of competing alkenes were mixed with precursors **3** or **4** in ratios that depended on the relative reactivity of the alkene pair. Additions were conducted by standard procedures, and product ratios were determined by integration of the ^{1}H NMR spectra of the crude reaction mixtures. Under conditions of irreversible addition, the product ratios in such experiments are direct measures of the relative reactivity of the alkene pair. We deliberately avoided reactions with (phenylseleno)malononitrile **4** and disubstituted alkenes **19** because radical additions are likely to be reversible and product ratios may not represent relative reactivities of the alkenes toward **19**.

Table 4. Relative Reactivities toward the Methylmalononitrile Radical (60 °C)

entry	**8** or **19**	method[a]	k_{rel}
1		2	33
2		1	30
3		2	24
4		2	16
5		1	5.2
6		1	2.9
7		1	≡1.0
8		1	0.32
9		1	0.10
10		1	0.03

[a] Method 1: thermolysis with iodomalononitrile **3**. Method 2: photolysis with (phenylseleno)malononitrile **4**.

Relative rate constants for addition of **11** vary over a range of about 10^3 M^{-1} s^{-1}. Radical **11** adds well to simple alkyl-substituted alkenes like 1-hexene, but additions to electron-poor alkenes like acrylonitrile and methyl acrylate are very slow (entries 9, 10). Alkenes are slightly more reactive than analogous alkynes (entry 8), and electron-rich alkenes like enol thioethers, enol ethers, and enamides are about 16–33-fold more reactive than 1-hexene (entries 1, 3, 4). Styrene is among the most reactive alkenes studied (k_{rel} = 30, entry 2). *trans*-β-Methylstyrene (entry 5) is only about 6-fold less reactive than styrene, while *cis*-β-methylstyrene (entry 6) is about 10-fold less reactive (which still makes it about 3-fold more reactive than 1-hexene).

Radical **11** exhibits a reactivity profile that is emerging as typical of an electrophilic radical.[12,29] Compared to nucleophilic radicals (like the *tert*-butyl radical[30]), the range of relative reactivities of **11** is somewhat compressed, especially when one considers rates above that of the common standard 1-hexene (the most reactive acceptor studied is only 33-fold more reactive than

(27) Malononitrile radical **7**, formed concomitantly with **3**, is reduced to methylmalononitrile (observed in the ^{1}H NMR spectra). Reduction of **6** by tin hydride competes with β-fragmentation. Since the hydrogen transfer rate constants for radicals like **6** are not known and since it is unclear if the β-elimination is reversible under these conditions, quantitative comparision of fragmentation rates of substrates with different R^2 groups is not possible.

(28) (a) Klenke, K.; Metzger, J. O.; Lübben, S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1168. (b) Metzger, J. O.; Klenke, K. *Chem. Ber.* **1990**, *123*, 875. (c) For related β-fragmentations at <150 °C, see: Huang, R. L.; Oog, C.-O.; Ong, S. H. *J. Chem. Soc. C* **1968**, 2217.

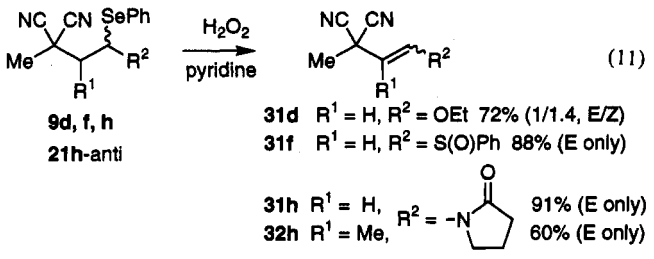
(29) (a) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753. (b) Zipse, H.; He, J.; Houk, K. N.; Giese, B. *J. Am. Chem. Soc.* **1991**, *113*, 4324. (c) Baciocchi, E.; Ruzziconi, R. *J. Org. Chem.* **1991**, *56*, 4772. (d) Gleicher, G. J.; Mahiou, B.; Aretakis, A. J. *J. Org. Chem.* **1989**, *54*, 308. This paper includes several competitions with the unsubstituted malononitrile radical. (e) Santi, R.; Bergamini, F.; Citterio, A.; Sebastiano, R.; Nicolini, M. *J. Org. Chem.* **1992**, *57*, 4250. (f) Heberger, K.; Fischer, H. *Int. J. Chem. Kinet.* **1993**, *25*, 249.

(30) (a) Jent, F.; Paul, H.; Roduner, E.; Heming, M.; Fischer, H. *Int. J. Chem. Kinet.* **1986**, *18*, 1113. (b) Fischer, H. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousak, Z., Merényi, R., Eds.; NATO ASI Series C; Reidel: Dordrecht, 1986; Vol. 189, pp 123.

1-hexene). This apparent compression is a consequence of choosing 1-hexene as a standard; 1-hexene is a relatively reactive partner in additions of electrophilic radicals and a relatively unreactive partner in additions of nucleophilic radicals. For the radical **11**, most of these relative rates agree with "polar effects" as interpreted by FMO theory.[29a] A key exception is the relative positioning of styrene, which is among the most reactive of alkenes. Contrast this to nucleophilic radical additions where styrene is 10–100 times less reactive than electron-poor alkenes.[29a] This observation supports the recent suggestion of Heberger and Fischer[29f] that enthalpy contributions to rate constants are more significant than is generally believed for electrophilic radicals.

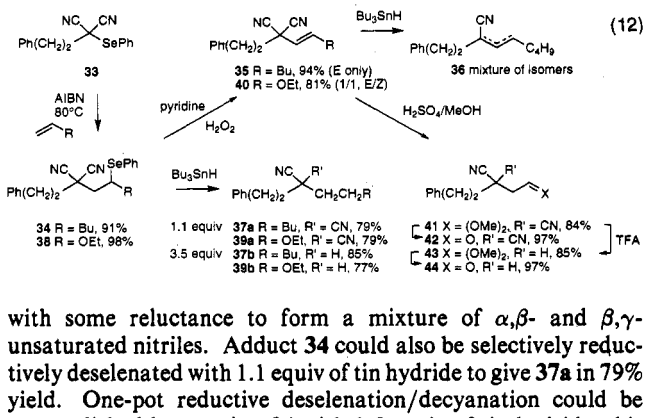
Transformations of the Products

We believe that the selenium transfer addition products prepared in this work have broad synthetic potential, and to illustrate this potential, we studied a series of representative transformations with a number of adducts. Several examples of selenoxide elimination of the phenylselenium group are shown in eq 11. Oxidation of adducts **9d**, **9f**, and **9h** under standard conditions (H_2O_2, pyridine)[31] provided alkenes **31d**, **31f**, and **31h** in good to excellent yields (72–91%). The enol ether **31d** was an *E*/*Z* mixture, while the enol phenyl sulfide **31f** and the enamide **31b** were exclusively *E*. Oxidation of *syn*-**21h** failed to provide an alkene, but oxidation and syn elimination of anti-**21h** occurred smoothly to produce *E*-**32h**. We developed additional transfor-



(11)

mations in the alkyl- and oxygen-series, as summarized in eq 12. Addition of **33** to 1-hexene provided **34** in 91% yield.[32] Oxidation and elimination then provided the *E*-alkene **35** as the only regioisomer in 94% yield. Reductive decyanation[33] of **35** occurred



(12)

with some reluctance to form a mixture of α,β- and β,γ-unsaturated nitriles. Adduct **34** could also be selectively reductively deselenated with 1.1 equiv of tin hydride to give **37a** in 79% yield. One-pot reductive deselenation/decyanation could be accomplished by treating **34** with 3.5 equiv of tin hydride; this gave mononitrile **37b** in 85% yield.

In the oxygen series, adduct **38** formed in excellent yield (98%) on addition of **33** to ethyl vinyl ether. Either monoreduction of **38** to give **39a** (79%) or double reduction to give **39b** (77%) was possible. Oxidation and phenylselenoxide elimination provided **40**, which surprisingly proved to be inert to tin hydride reductive decyanation. However, **40** was smoothly converted to the dimethyl acetal **41** on treatment with sulfuric acid in methanol. Hydrolysis of this acetal provided the β,β-dicyanoaldehyde **42** in 97% yield. Reductive decyanation of **41** was successful and gave **43** in 85% yield. Further TFA hydrolysis provided β-cyanoaldehyde **44** in 97% yield.

Conclusions

The chemistry of (phenylseleno)malononitriles reported in the paper increases our understanding of this relatively unexplored class of molecules, and it broadens the synthetic usefulness of the atom/group transfer method in at least three directions. First, compared to iodomalononitriles, these new phenylselenium reagents significantly expand the scope of the alkene partners for such electrophilic radical additions by including large, important classes of electron-rich alkenes. Second, the good to excellent stereoselectivities exhibited in the selenium transfer reaction may be useful of themselves (for example in stereoselective selenoxide eliminations), and they also suggest that related stereoselective C–X, C–H, and C–C bond forming reactions could be developed. Direct applications with these adducts are limited by the propensity for malononitrile radical elimination. However, indirect applications are readily envisioned by replacing the malononitrile group with another large group that will resist radical fragmentation. Third, the products of these phenylselenium transfer reactions are much more synthetically versatile than products of related halogen and hydrogen transfer reactions. Equations 11 and 12 begin to show some of this versatility, and we believe that many more useful transformations can also be developed.

Experimental Section

Methyl(phenylseleno)propanedinitrile (Methyl(phenylseleno)malonodinitrile) (4). A solution of methylmalonodinitrile (1.00 g, 12.5 mmol) in THF (20 mL) was added under argon at −10 °C to a suspension of oil-free NaH (18.8 mmol, obtained from 0.75 g of 60% NaH suspension in mineral oil) in THF (20 mL). The reaction mixture was warmed to 25 °C over 1 h and then cooled to −30 °C. A solution of phenylselenenyl bromide (4.42 g, 18.8 mmol) in THF (20 mL) was added over 10 min. The reaction mixture was slowly warmed to 25 °C, stirred for 16 h, diluted with ether (100 mL), and extracted with NaCl solution (2 × 50 mL), 1N HCl, (2 × 50 mL), and water (50 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. Flash chromatography (silica gel ether/pentane 1/9) gave 2.25 g (77%) of methyl(phenylseleno)malonodinitrile (**4**) as a pale yellow solid, mp 71–72 °C: ^{1}H NMR ($CDCl_3$) δ 7.89–7.47 (5 H, m), 2.06 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 137.6 (2 C), 131.7, 129.9 (2 C), 125.0, 114.9 (2 C), 24.3, 20.0; IR (neat) 3070, 2990, 2240, 1475, 1450, 1175 cm^{-1}; MS *m*/*e* (M^+) 236, 157, 117, 105, 77; HRMS calc for $C_{10}H_8N_2{}^{76}Se$ 233.9861, found 233.9861.

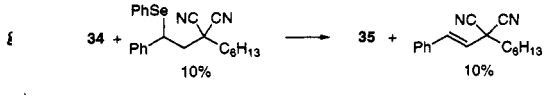
General Procedure for Group Transfer Addition Reactions of 4. A chloroform (or benzene) solution of **4** (0.1 M), an alkene (2 equiv), and AIBN (0.05 equiv) was heated under nitrogen at 60 °C (or 80 °C in benzene) for the time period indicated in Table 1 or Table 2. The solvent was removed, and the crude product was purified by flash chromatography. Isolated yields and product ratios are found in Tables 1 and 2, and spectroscopic data are listed below.

(2-(Phenylseleno)hexyl)methylpropanedinitrile (9a): ^{1}H NMR ($CDCl_3$) δ 7.61–7.28 (5 H, m), 3.37 (1 H, br quint), 2.28 (2 H, m), 1.95–1.31 (6 H, m), 1.77 (3 H, s), 0.92 (3 H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 135.5 (2 C), 129.3 (2 C), 128.4, 127.4, 116.3, 115.7, 44.3, 41.1, 34.3, 30.9, 29.5, 26.1, 22.2, 13.9; IR (neat) 3061, 2959, 2932, 2860, 2245, 1117, 1477, 1464, 1437, 740, 691 cm^{-1}; MS *m*/*e* 320 (M^+) 158, 96, 77; HRMS calc for $C_{16}H_{20}N_2Se$ 320.0792, found 320.0792.

(2-(Phenylseleno)-2-phenylethyl)methylpropanedinitrile (9c): ^{1}H NMR ($CDCl_3$) δ 7.65–6.90 (10 H, m), 4.55 (1 H, dd, *J* = 11.3, 3.8 Hz), 2.76 (1 H, dd, *J* = 14.3, 11.3 Hz), 2.47 (1 H, dd, *J* = 14.3, 3.8 Hz), 1.61 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 138.4, 135.3 (2 C), 129.4 (2 C), 129.0 (2

(31) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.

(32) On a small scale (several hundred milligrams), this reaction worked very cleanly. On a large scale (several grams), **34** was accompanied by about 10% of the inseparable product shown below, which results from 1,5-hydrogen transfer. Oxidation of this mixture gave **35** and the corresponding styrene.



(33) Curran, D. P.; Seong, C. M. *Synlett* **1991**, 107.

C), 128.7, 128.6, 128.3, 128.1 (2 C), 115.5, 114.8, 44.3, 43.2, 31.2, 25.8; IR (neat) 3060, 3040, 2950, 2940, 2240, 1785, 1690, 1580, 1475, 1455, 1435 cm^{-1}; MS *m/e* 183 $(M - 157)^+$, 157, 104, 91, 77; HRMS for $C_{18}H_{16}N_2Se$ 340.0479, found 340.0479.

(2-Ethoxy-2-(phenylseleno)ethyl)methylpropanedinitrile (9d): ^1H NMR ($CDCl_3$) δ 7.65–7.32 (5 H, m), 5.70 (1 H, dd, J = 9.0, 4.9 Hz), 4.08 (1 H, dq, J = 9.3, 7.0 Hz), 3.56 (1 H, dq, J = 9.3, 7.0 Hz), 2.45 (2 H, m), 1.77 (3 H, s), 1.33 (3 H, t, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$)$_5$ 135.9, 129.3 (2 C), 128.5 (2 C), 126.4, 116.0, 115.7, 80.7, 66.2, 45.7, 30.3, 25.6, 14.2; IR (neat) 3059, 2978, 2878, 2249, 1475, 1437, 1157, 1113, 1066, 1022 cm^{-1}; MS *m/e* 308 (M^+), 183, 151, 123; HRMS calc for $C_{14}H_{16}N_2OSe$ 308.0428, found 308.0428.

(2-Acetoxy-2-(phenylseleno)ethyl)methylpropanedinitrile (9e): ^1H NMR ($CDCl_3$) δ 7.65–7.33 (5 H, m), 6.44 (1 H, dd, J = 11.0, 2.8 Hz), 2.54 (1 H, dd, J = 14.8, 11.0 Hz), 2.41 (1 H, dd, J = 14.8, 2.8 Hz), 2.15 (3 H, s), 1.77 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 169.0, 136.5 (2 C), 129.5 (2 C), 129.4, 125.1, 115.5, 114.9, 67.8, 44.1, 29.7, 25.1, 20.9; IR (neat) 3060, 2995, 2251, 1754, 1578, 1476, 1439, 1211, 1020, 741, 692 cm^{-1}; MS *m/e* 322 (M^+), 263, 200, 158, 77; HMRS calc for $C_{14}H_{14}N_2O_2Se$ 322.0221, found 322.0221.

(2-(Phenylseleno)-2-(phenylthio)ethyl)methylpropanedinitrile (9f): ^1H NMR ($CDCl_3$) δ 7.64–7.23 (10 H, m), 4.58 (1 H, dd, J = 8.2, 6.2 Hz), 2.51 (1 H, dd, J = 15.1, 8.2 Hz), 2.45 (1 H, dd, J = 15.1, 6.2 Hz), 1.79 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 135.6 (2 C), 133.1 (2 C), 133.0, 129.5 (2 C), 129.4 (2 C), 129.1, 128.8, 128.0, 115.8, 115.6, 46.3, 44.2, 31.2, 26.1; IR (neat) 3030, 2950, 2790, 2250, 1580, 1490, 1440, 1300, 1220, 1150, 1000 cm^{-1}; MS *m/e* 372 (M^+), 215, 136; HRMS calc for $C_{12}H_{11}N_2S$ (M – PhSe) 215.0637, found 215.0636.

(2-(*N*-Imidazolinyl)-2-(phenylseleno)ethyl)methylpropanedinitrile (9g): ^1H NMR ($CDCl_3$) δ 7.65–7.05 (8 H, m), 5.67 (1 H, dd, J = 10.4, 4.2 Hz), 2.84 (1 H, dd, J = 14.7, 10.4), 2.73 (1 H, dd, J = 14.7, 4.2), 1.72 (3 H, s); ^{13}C NMR ($CDCl_{13}$) δ 136.1 (2 C), 131.0, 130.0, 129.7 (2 C), 129.5, 129.4, 125.7, 114.8, 113.8, 53.0, 44.2, 29.7, 25.1; IR (neat) 3110, 2920, 2245, 1690, 1490, 1475, 1440, 1225, 1105, 1080 cm^{-1}; MS *m/e* 330 (M^+), 251, 173, 94, 77, 67; HRMS calc for $C_{15}H_{14}N_4Se$ 330.0384, found 330.0383.

(2-(*N*-(2-pyrrolidonyl))-2-(phenylseleno)ethyl)methylpropanedinitrile (9h): Mp 82–83 °C; ^1H NMR ($CDCl_3$) δ 7.58–7.27 (5 H, m), 6.07 (1 H, dd, J = 12.5, 2.7 Hz), 3.45 (2 H, m), 2.84 (1 H, dd, J = 14.4, 12.5 Hz), 2.35–1.75 (4 H, m), 2.31 (1 H, dd, J = 14.4, 2.7 Hz), 1.84 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 175.8; 135.4 (2 C), 129.2 (2 C), 128.8, 126.4, 115.7, 115.0, 49.3, 43.2, 39.9, 30.6, 29.5, 23.8, 17.1; IR (neat) 2960, 2870, 2240, 1680, 1580, 1420, 1300, 1270, 1230, 1220, 740; MS *m/e* 190 $(M^+ - 157)$, 163, 157, 111, 69; HRMS calc for $C_{10}H_{12}N_3O$ $(M^+ - PhSe)$ 190.0980, found 190.0980.

(2-(*N*-Carbazolyl)-2-(phenylseleno)ethyl)methylpropanedinitrile (9i): ^1H NMR δ 8.10–6.99 (13 H, m), 6.47 (1 H, dd, J = 11.2, 3.4 Hz), 3.57 (1 H, dd, J = 14.6, 11.2 Hz), 2.87 (1 H, dd, J = 14.6, 3.4 Hz), 1.54 (3 H, s); ^{13}C NMR 140.4, 137.9, 136.1 (2 C), 129.1 (2 C), 126.9, 126.3, 125.7, 125.3, 123.0, 120.9, 120.7, 120.3, 115.4, 114.3, 112.4, 108.8, 52.8, 42.2, 31.0, 24.6; IR (neat) 3057, 2930, 2249, 1597, 1483, 1449, 1329, 1223, 1159, 750 cm^{-1}; MS *m/e* 429 (M^+), 272, 193, 166; HRMS calc for $C_{24}H_{19}N_3Se$ 429.0744, found 429.0744.

(2-(Phenylseleno)-6-heptenyl)methylpropanedinitrile (9j). 9j was isolated as a mixture with **18**: ^1H NMR ($CDCl_3$) δ 7.65–7.25 (5 H, m), 5.79 (1 H, m), 5.01 (2 H, m), 3.73 (1 H, dq, J = 4.4, 7.5 Hz), 2.10–1.55 (8 H, m), 1.87 (3 H, s); MS *m/e* 332 (M^+), 158, 156, 108, 95, 77.

cis- and trans ((2-((Phenylseleno)methyl)cyclopentyl)methyl)methylpropanedinitrile (*cis*-18 and *trans*-18). 18 was isolated as a mixture with **9j**. *cis*-**18**: ^1H NMR 7.65–7.25 (5 H, m); 2.89 (1 H, dd, J = 11.4, 5.4 Hz), 2.75 (1 H, dd, J = 11.4, 9.3 Hz), 2.35–1.55 (10 H, m), 1.87 (3 H, s); MS *m/e* 332 (M^+), 158, 156, 108, 95, 77. *trans*-**18**: ^1H NMR 7.65–7.25 (5 H, m), 3.09 (1 H, dd, J = 11.9, 4.9 Hz), 2.91 (1 H, dd, J = 11.9, 8.0 Hz), 2.35–1.55 (10 H, m), 1.90 (3 H, s); MS *m/e* 332 (M^+), 158, 156, 108, 95, 77.

(2-(Phenylseleno)cyclopentyl)methylpropanedinitrile (*trans*-21a): ^1H NMR ($CDCl_3$) δ 7.62–7.31 (5 H, m), 3.54 (1 H, quint, br, J = 4.0 Hz), 2.40 (1 H, td, J = 8.0, 4.5 Hz), 2.20 (2 H, m), 1.97–1.63 (4 H, m), 1.76 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 135.2 (2 C), 129.4 (2 C), 129.0, 128.4, 115.9, 115.6, 53.1, 43.0, 35.7, 31.0, 29.0, 24.9, 24.1; IR (neat) 2955, 2870, 2250, 1735, 1575, 1470, 1250, 1210, 1050 cm^{-1}; MS *m/e* 304 (M^+), 227, 158, 91, 78, 67; HRMS calc for $C_{15}H_{16}N_2Se$ 304.0479, found 304.0475.

2-(3-(Phenylseleno)tetrahydropyranyl)methylpropanedinitrile (21b). *trans*-**21b**: ^1H NMR ($CDCl_3$) δ 7.63–7.27 (5 H, m), 5.89 (1 H, s, br), 4.24 (1 H, m) 3.83 (1 H, m), 2.37 (1 H, m), 2.26–2.09 (3 H, m), 1.89 (3 H, s), 1.65 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 134.2 (2 C), 129.4 (2 C), 129.0, 128.2, 116.0, 115.8, 82.4, 65.8, 62.1, 46.1, 34.3, 24.3, 22.1; IR (neat) 3050, 2970, 2880, 2250, 1660, 1475, 1255, 1090, 1060, 1020, 800 cm^{-1}; MS *m/e* 370 (M^+), 163, 84, 55; HRMS calc for $C_9H_{11}N_2O$ $(M^+ - SePh)$ 163.0871, found 163.0871. *cis*-**21b**: ^1H NMR ($CDCl_3$) δ 7.67–7.23 (5 H, m), 5.76 (1 H, dd, J = 4.1, 1.9 Hz), 4.27 (1 H, m), 3.84 (1 H, m), 2.37 (1 H, m), 2.03 (1 H, m), 1.90 (3 H, s), 1.91–1.77 (3 H, m); ^{13}C NMR ($CDCl_3$) δ 134.5 (2 C), 129.3 (2 C), 128.8, 128.2, 115.6, 114.8, 87.0, 61.4, 48.0, 35.2, 25.2, 23.6, 23.4; IR (neat) 3060, 2990, 2860, 2240, 1080, 1530, 1490, 1200, 1100, 870, 830 cm^{-1}; MS *m/e* 163 $(M^+ - 157)$, 84, 55.

(1-Methyl-2-(phenylseleno)-2-phenylethyl)methylpropanedinitrile (21c). 21 was isolated as a mixture. *syn*-**21c**: ^1H NMR ($CDCl_3$) δ 7.75–7.10 (10 H, m), 4.53 (1 H, d, J = 6.5 Hz), 2.52 (1 H, quint, J = 6.5 Hz), 1.74 (3 H, s), 1.47 (3 H, d, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 140.7, 135.0 (2 C), 129.0 (2 C), 128.9 (2 C), 128.7, 128.6, 128.5, 128.1, 127.8, 115.7, 115.5, 52.8, 46.9, 37.1, 24.5, 14.7; MS *m/e* 354 (M^+), 264, 197, 157, 118, 105, 91, 77; HRMS calc for $C_{19}H_{18}N_2Se$ 354.0635, found 354.0628. *anti*-**21c**: ^1H NMR ($CDCl_3$) δ 7.75–7.10 (10 H, m), 4.88 (1 H, d, J = 4.0 Hz), 2.38 (1 H, dq, J = 7.1, 4.0 Hz), 1.69 (3 H, s), 1.52 (3 H, d, J = 7.1 Hz); MS *m/e* 354 (M^+), 264, 197, 157, 118, 105, 91, 77.

(1-Methyl-2-phenylethyl)methylpropanedinitrile (22c): ^1H NMR ($CDCl_3$) δ 7.56–7.16 (5 H, br, m), 3.21 (1 H, dd, J = 13.1, 2.9 Hz), 2.47 (1 H, dd, J = 13.1, 11.4 Hz), 2.18 (1 H, ddq, J = 11.4, 2.4, 6.6 Hz), 1.81 (3 H, 5), 1.07 (3 H, d, J = 6.6 Hz).

(2-Ethoxy-2-(phenylseleno)-1-methylethyl)methylpropanedinitrile (21e). 21e was isolated as a mixture. *syn*-**21e**: ^1H NMR ($CDCl_3$) δ 7.65–7.30 (5 H, m), 5.40 (1 H, d, J = 2.1 Hz), 3.94 (1 H, dq, J = 9.1, 7.0 Hz), 3.41 (1 H, dq, J = 9.1, 7.0 Hz), 2.49 (1 H, dq, J = 7.0, 2.1 Hz), 1.79 (3 H, s), 1.47 (3 H, d, J = 7.0 Hz), 1.25 (3 H, t, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 135.0 (2 C), 129.5 (2 C), 129.3, 128.3, 116.5, 115.8, 89.9, 66.9, 47.8, 35.5, 23.7, 14.2, 10.6; MS *m/e* 322 (M^+), 165, 137, 109, 94, 77; HRMS calc for $C_{15}H_{18}N_2OSe$ 322.0584, found 322.0575. *anti*-**21e**: ^1H NMR ($CDCl_3$) δ 7.65–7.30 (5 H, m), 4.75 (1 H, d, J = 9.2 Hz), 4.16 (1 H, dq, J = 8.8, 1.8 Hz), 3.48 (1 H, dq, J = 8.8, 1.8 Hz), 2.29 (1 H, dq, J = 9.2, 6.9 Hz), 1.76 (3 H, s), 1.34 (3 H, t, J = 6.9 Hz), 1.33 (3 H, d, J = 6.9 Hz); MS *m/e* 322 (M^+), 165, 137, 109, 94, 77.

(2-Phenoxy-2-(phenylseleno)-1-methylethyl)methylpropanedinitrile (21f). 21f was isolated as a mixture. *syn*-**21f**: ^1H NMR ($CDCl_3$) δ 7.47–6.98 (10 H, m), 6.07 (1 H, d, J = 2.0 Hz), 2.64 (1 H, dq, J = 2.0, 7.0 Hz), 1.80 (3 H, s), 1.66 (3 H, d, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 155.5, 135.3 (2 C), 129.7, 129.5 (4 C), 128.7, 123.2, 117.3 (2 C), 115.5, 115.2, 84.7, 47.6, 35.4, 23.2, 10.7. *anti*-**21f**: ^1H NMR ($CDCl_3$) δ 7.51–7.00 (10 H, m), 5.58 (1 H, d, J = 9.1 Hz), 2.49 (1 H, dq, J = 9.1, 7.0 Hz), 1.80 (3 H, s), 1.47 (3 H, d, J = 7.0 Hz), ^{13}C NMR ($CDCl_3$) δ 155.1, 136.2 (2 C), 129,3 (2 C), 128.9, 128.1 (2 C), 125.7, 123.1, 116.9 (2 C), 115.5, 115.3, 83.5, 45.1, 34.1, 23.5, 14.2; MS *m/e* 370 (M^+), 277, 213, 198, 157, 134, 84; HRMS calc for $C_{13}H_{13}N_2O$ $(M^+ - PhSe)$ 213.1028, found 213.1028.

(2-(Phenylseleno)-2-(phenylthio)-1-methylethyl)methylpropanedinitrile (21g). 21g was isolated as a mixture. *syn*-**21g**: ^1H NMR ($CDCl_3$) δ 7.65–7.24 (10 H, m), 4.75 (1 H, d, J = 2.3 Hz), 2.24 (1 H, dq, J = 2.3, 6.8 Hz), 1.76 (3 H, 5), 1.51 (3 H, d, J = 6.8 Hz); MS *m/e* 386 (M^+), 229, 157. *anti*-**21g**: ^1H NMR ($CDCl_3$) δ 7.65–7.24 (10 H, m), 4.91 (1 H, d, J = 7.4 Hz), 2.29 (1 H, dq, J = 2.4, 7.1 Hz), 1.75 (3 H, s), 1.58 (3 H, d, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 134.8 (2 C), 132.6 (2 C), 132.4, 129.6 (2 C), 129.5, 129.4 (2 C), 128.8, 128.6, 115.6, 115.4, 55.5, 45.6, 36.0, 24.2, 11.5; MS *m/e* 386 (M^+), 229, 166, 150, 123, 109, 99, 84; HRMS calc for $C_{13}H_{13}N_2S$ $(M^+ - PhSe)$ 229.0786, found 229.078 86.

(2-(Phenylthio)-1-methylethyl)methylpropanedinitrile (22g): ^1H NMR ($CDCl_3$) δ 7.60–7.30 (5 H, m), 3.40 (1 H, dd, J = 13.4, 2.3 Hz), 2.71 (1 H, dd, J = 13.4, 11.1 Hz), 2.08 (1 H, m), 1.74 (3 H, s), 1.31 (3 H, d, J = 7.0 Hz).

(2-(*N*-(2-Pyrrolidonyl))-2-(phenylseleno)-1-methylethyl)methylpropanedinitrile (21h). *syn*-**21h**: ^1H NMR ($CDCl_3$) δ 7.56–2.26 (5 H, m), 5.93 (1 H, d, J = 11.2 Hz), 3.49 (2 H, m), 2.82 (1 H, dq, J = 11.2, 7.0 Hz), 2.25–1.40 (5 H, m), 1.82 (3 H, s), 1.41 (3 H, d, J = 7.0 Hz); ^{13}C NMR 176.3, 135.8 (2 C), 129.2 (2 C), 128.8, 126.5, 116.3, 115.8, 56.5, 43.7, 41.3, 34.4, 30.4, 19.5, 16.7, 15.2; IR (neat) 3060, 2980, 2250, 1690, 1405, 1285 cm^{-1}; HRMS calc for $C_{11}H_{14}N_3O$ $(M^+ - PhSe)$ 204.1134, found 204.1135. *anti*-**21h**: ^1H NMR ($CDCl_3$) δ 7.56–7.25 (5 H, m), 6.25 (1 H, d, J = 3.4 Hz), 3.72 (1 H, dt, J = 9.1, 4.7 Hz), 3.56 (1 H, dt, J = 9.1, 7.3 Hz), 2.54 (1 H, dq, J = 3.4, 7.2 Hz), 2.32–1.54 (4 H, m), 1.99 (3 H, s), 1.64 (3 H, d, J = 7.3 Hz); ^{13}NMR ($CDCl_3$) δ 176.6, 135.3 (2 C), 129.4 (2 C), 128.9, 126.4, 116.2, 114.7, 54.7, 46.3, 45.9, 36.0, 30.2, 22.9, 18.6, 15.3; IR (neat) 3050, 2985, 2250, 1690, 1400, 1230

cm^{-1}; MS *m/e* 204 $(M - 157)^+$, 177, 157, 125, 70, 47; HRMS calc for $C_{11}H_{14}N_3O$ (M^+ – PhSe) 204.1134, found 204.1135.

(2-(*N*-Carbazolyl)-2-(phenylseleno)-1-methylethyl)methylpropanedinitrile (21i). *syn*-**21i**: mp 127–128 °C; ^1H NMR ($CDCl_3$) δ 8.10–6.90 (13 H, m), 6.32 (1 H, d, *J* = 10.6 Hz), 3.56 (1 H, dq, *J* = 10.6, 6.9 Hz), 1.75 (3 H, d, *J* = 6.9 Hz), 1.34 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 140.4, 138.3, 136.8 (2 C), 128.9, 128.4 (2 C), 126.1, 125.7, 125.5, 125.2, 122.7, 120.7, 120.6, 120.1, 119.9, 115.5, 114.6, 113.4, 109.0, 59.6, 43.7, 36.7, 23.5, 17.2; IR (neat) 3055, 2920, 2850, 2250, 1600, 1490, 1450, 1320, 1260, 1160; MS *m/e* 443 (M^+), 315, 286, 207; HRMS calc for $C_{19}H_{16}N_3$ (M^+ – PhSe) 286.1340, found 286.1344. Data of *anti*-**21i** were obtained from a mixture with *syn*-**21i**: ^1H NMR ($CDCl_3$) δ 8.10–6.90 (13 H, m), 5.99 (1 H, d, *J* = 9.8 Hz), 3.32 (1 H, dq, *J* = 9.8, 6.9 Hz), 1.26 (3 H, s), 1.00 (3 H, d, *J* = 6.9 Hz); MS *m/e* 443, 315, 286, 207.

(2-(*N*-Carbazolyl)-1-methylethyl)methylpropanedinitrile (22i): ^1H NMR ($CDCl_3$) δ 8.15–6.96 (8 H, m), 4.73 (1 H, dd, *J* = 14.8, 3.8 Hz), 4.37 (1 H, dd, *J* = 14.8, 10.7 Hz), 2.73 (dd, q, *J* = 10.7, 3.8, 8.8 Hz), 1.89 (3 H, s), 1.10 (3 H, d, *J* = 6.8 Hz).

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Supplementary Material Available: Details of the crystal structure of *anti*-**21h** and experimental procedures and characterizations for all the transformations and compounds shown in eqs 11 and 12 (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.