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RADICAL ADDITION OF VARIED FUNCTIONALITY VIA PHENYLSELENENYL TRANSFER

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Abstract: Simple phenylselenenyl ketones, esters, nitriles, and sulfones were added to octene upon photolysis. These addition reactions illustrate that the process of carbon-carbon bond formation accompanied by phenylselenenyl transfer possesses more general applicability than has previously been demonstrated or suspected.

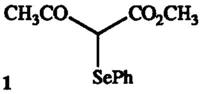
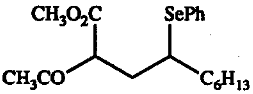
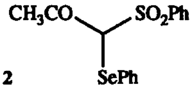
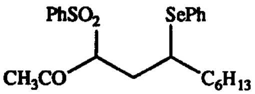
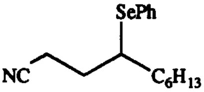
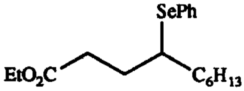
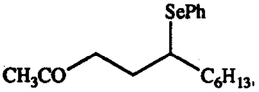
Several interesting and synthetically valuable transformations in the organic chemistry of free-radicals have involved the use of atom transfer methods, and iodine transfer in particular.[1] We recently demonstrated the first examples of carbon-carbon bond formation accompanied by phenylselenenyl transfer. In these studies, we showed that diethyl (2-phenylselenenyl)propanedioate could be added to a variety of simple olefins,[2] and that a variety of phenylselenenyl ß-dicarbonyl compounds could undergo hexenyl radical cyclizations.[3] More recently, Curran[4] has demonstrated the effectiveness of 2-phenylselenenyl malononitriles in radical addition reactions.

We report herein the addition reactions of a wider variety of organoselenides to a simple olefin, 1-octene. These reactions are summarized in the accompanying table.

Under typical reaction conditions, 0.33 mmol of octene and 1 mmol of the selenide were dissolved in 2 mL of benzene in a 5-mL round bottomed flask equipped with a condenser. The solution was degassed with bubbling Ar for 15 min, and photolyzed with a 275-W sunlamp until all octene was consumed, as monitored by gas chromatography. The yields shown are for products isolated by flash chromatography or MPLC. All addition products were fully characterized by ^{1}H and ^{13}C NMR, IR, MS, and combustion analysis.

The success achieved in the addition reactions of selenides 1 and 2[5] is not particularly surprising, given the known facility with which the electronically analogous phenylselenenyl malonic esters and malononitriles undergo radical addition reactions of this type. The addition of 1 or 2 to octene generated a roughly 50:50 mixture of diastereomers, as might be expected. These examples do, however, serve to exemplify further synthetic generality in the phenylselenenyl transfer radical additions.

The successful addition reactions of selenides 3[6], 4[7], and 5[8], however, are noteworthy not only for their further exemplification of the synthetic versatility of this methodology, but also for their mechanistic significance. We had assumed that these selenides, whose C-Se bond is presumably stronger than that in the selenenyl malonates and other electronically similar compounds, would not prove to be valuable reagents, due to less efficient initiation and a decreased rate of phenylselenenyl transfer. This assumption was further supported by the very slow rate and low yield reported[3] for the radical cyclization of N,N-diallyl-1-phenylselenenylacetamide which presumably proceeded via a radical stabilized by only one adjacent carbonyl. Somewhat surprisingly, selenides 4 and 5 were added to octene in good yield, albeit much more slowly than did 1 or 2, frequently requiring several days to completely consume the limiting reagent, octene. The addition of nitrile 3 proceded somewhat faster than the other cases studied, further illustrating the previously observed ability of the nitrile functionality to promote atom-transfer reactions, analogous to what has been noted in reactions of malononitrile radicals.[1a,1b,4]

STARTING SELENIDE	PRODUCT	YIELD (%)	REACTION TIME (HR)
 1		78	42
 2		77	24
$NCCH_2SePh$ 3		50	16
EtO_2CCH_2SePh 4		55	60
CH_3COCH_2SePh 5		72	60

Thus, free-radical carbon-carbon bond formation via phenylselenenyl transfer has been shown to be a more general process than has been previously demonstrated. In particular, organoselenides possessing only one radical-stabilizing functional group can be added to olefins.

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References and Notes

1. Several recent examples with leading references: (a) Curran, D. P.; Seong, C. M.; *Tetrahedron*, **1992**, *48*, 2157. (b) Curran, D. P.; Seong, C. M.; *Tetrahedron*, **1992**, *48*, 2175. (c) Curran, D. P.; Chen, M. -H.; Kim, D. *J. Am. Chem. Soc.* **1989**, *111*, 6265 (d) Curran, D. P. Chang, C. -T. *J. Org. Chem.* **1989**, *54*, 3140.
2. Byers, J. H.; Lane, G. C. *Tetrahedron Lett.* **1990**, 5697.
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5. Selenides **1** and **2** were synthesized from methyl acetoacetate and methyl phenylsulfonylacetate, respectively using an adaptation of a procedure described in: Renga, J. M. Reich, H. J. *Org. Syn.* **1980**, *59*, 58.
6. Detty, M. R.; Wood, G. P. *J. Org. Chem.* **1980**, *45*, 80. As the cited procedure did not give satisfactory yields of **3**, it was instead synthesized by addition of PhSeSePh and $NaBH_4$ to a solution of chloroacetonitrile in EtOH.
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