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ON THE DIRECT GENERATION OF EPISELENONIUM IONS FROM ALKENES. AN EFFICIENT NEW PROCEDURE FOR EFFECTING SELENYLATIVE ARENE-ALKENE CARBOANNULATIONS.

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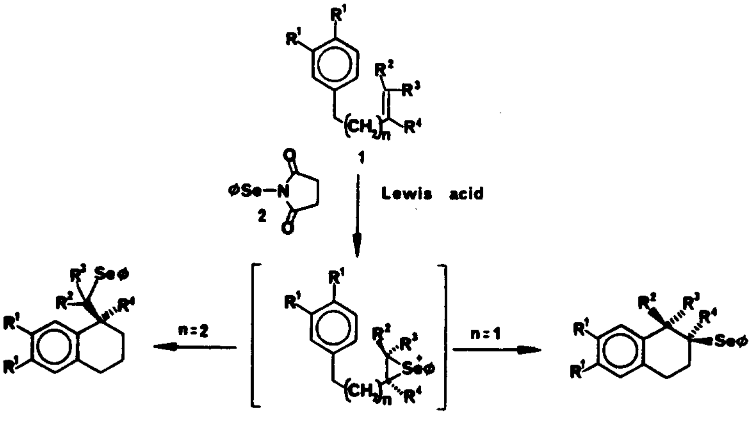
Abstract: The treatment of a variety of 2-(aryl)pent-4-enenitriles with N-(phenylseleno)succinimide (PSS) in the presence of Lewis acids gives rise to the corresponding (phenylseleno)tetralin derivatives in good to excellent overall yield.

Recently, we reported a new method for the generation of episulfonium ions and described its utility for effecting cationic carboannulations.[1] The synthetic uses of the phenylseleno moiety strongly complement those of the phenylthio group.[2-4] We now report that carboannulations accompanied by the introduction of the phenylseleno function can be achieved in high yield by the exposure of appropriate olefinic substrates to N-(phenylseleno)succinimide 2 (PSS)[5] in the presence of Lewis acids.[6]

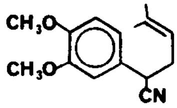
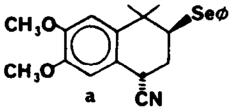
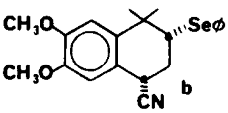
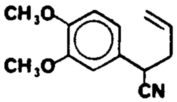
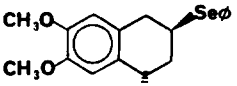
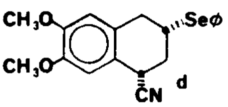
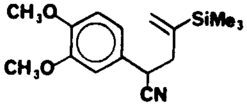
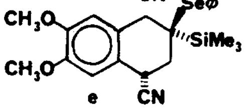
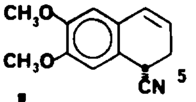
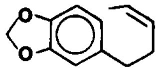
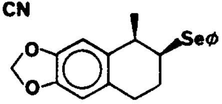
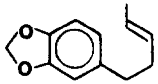
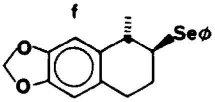
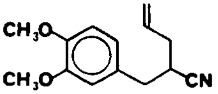
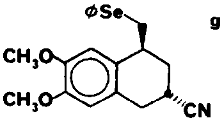
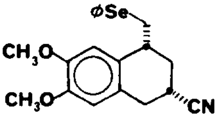
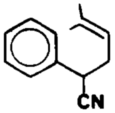
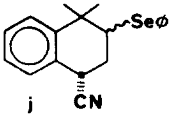
In a typical experiment, a solution of 1.05 equiv. of PSS 2 dissolved in CH_2Cl_2 was cooled to -78 °C and treated with the specified amount of a Lewis acid. After stirring for 2 min, a CH_2Cl_2 solution of the precyclization substrate 1 was added and the mixture was then stirred for 2 h at -78 °C and then stored for 16 h at -20 °C. Neutralization of the reaction mixture (aq. $NaHCO_3$) followed by chromatographic purification provided the cyclized products 4a-i.[7] The results obtained from a comprehensive study of episelenonium ion initiated arene-alkene cyclizations are summarized in **Table I.**



4h,i 3 4a-g

TABLE I

PSS-Lewis Acid Mediated Selenylative Carboannulations

	Substrate 1	Lewis Acid (eq)	Products 4		Ratio / Yield (%)
a		BF_3 (2.10) TMSOTf (2.10) $SnCl_4$ (1.05)	 a	 b	1.0 : 1.4 (92) 1.0 : 3.0 (94) 1.0 : 3.6 (92)
b		BF_3 (2.10) TMSOTf (2.10) $SnCl_4$ (1.05)	 c	 d	1.2 : 1.0 (74) 1.0 : 1.4 (80) 1.0 : 1.3 (78)
c		TMSOTf (2.10)	 e	 5	6.6 : 1.0 (61)
d		TMSOTf (2.10)	 f		(91)
e		TMSOTf (2.10)	 g		(86)
f		TMSOTf (2.10) $SnCl_4$ (1.05)	 h	 i	2.6 : 1.0 (90) 2.0 : 1.0 (88)
g		TMSOTf (2.10)	 j		(0)

As is evident from the results presented above, PSS-Lewis acid binary systems are quite useful for the initiation of efficient carbocycle annulations in a wide range of substrates. It is noteworthy that the product yields obtained from episelenonium ion carboannulations are typically higher than those observed for corresponding cyclizations involving episulfonium ions.[1] In consonance with our previous results[1], the cyclization of the substrates **1a-e** gave rise to the exclusive formation of products derived from the exo-mode of episelenonium ion bond scission (e.g. **4a-g**). Moreover, treatment of the E- and Z-alkenes **1d** and **e** with PSS-TMSOTf led to the stereospecific formation of the corresponding trans- and cis- tetralin derivatives **4f** and **4g**.[8] The latter result provides chemical evidence for the existence of episelenonium ions as transient intermediates in the preceeding reactions. It is of interest that the vinylsilane **1c** undergoes selenylative cyclization with reasonable efficiency to provide the diastereomerically pure bicyclic intermediate **4e** in 53% isolated yield.[8] All previous efforts to effect an analogous cyclization of **1c** using $PhSOCH_3$ in combination with Lewis acids met with failure.[9] By way of contrast, the substrate **1g** (which bears a nonactivated aryl terminator) underwent cyclization in 47% yield in the presence of $PhSOCH_3$ and 2 equiv. of BF_3 while the use of the PSS-Lewis acid procedures furnished only uncyclized products in low yield.[10]

The utility of N-(phenylseleno)succinimide (PSS) **2** in conjunction with Lewis acids for effecting selenylative carboannulations has been established. This procedure is complementary to episulfonium[1] and mercuronium ion[11] initiated cyclizations and should suggest new applications of cationic annulations to problems of synthetic interest. The utilization of episulfonium and episelenonium ion initiated polyene cyclizations for the construction of naturally occurring ring systems will be the topic of future accounts from these laboratories.

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