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AN EXAMINATION OF THE SYNTHETIC UTILITY OF PHENYLSELENENYL CHLORIDE ADDITIONS TO OLEFINS[1]

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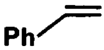
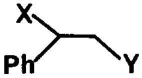
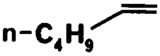
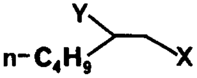
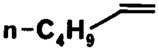
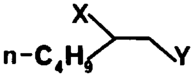
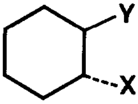
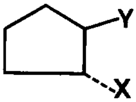
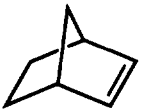
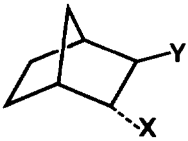
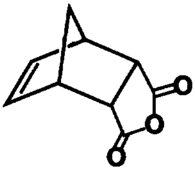
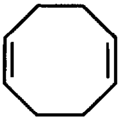
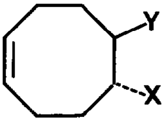
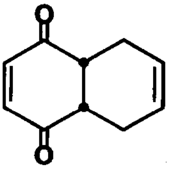
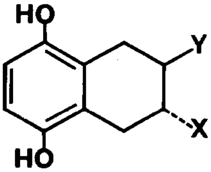
Although the additions of PhSeX reagents (X = Cl, Br, O_2CCH_3, O_2CCF_3) to double bonds are potentially useful reactions, they have received little attention by synthetic chemists. In the cases of $PhSeO_2CCH_3$[2a] and $PhSeO_2CCF_3$[2b,c], this is probably due to the low regiospecificity of the additions. On the other hand the infrequent use of PhSeBr and PhSeCl additions to olefins is unquestionably related to the lack of data regarding the regiospecificity of the additions[3a,b] as well as the thermal and solvolytic stabilities of the resulting adducts[2a].

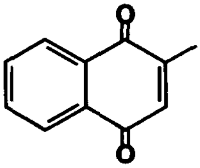
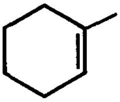
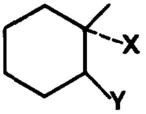
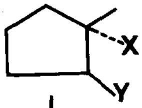
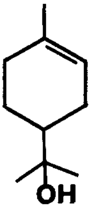
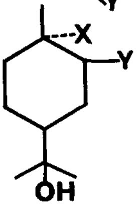
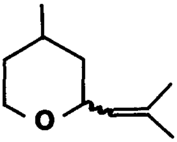
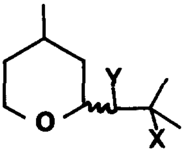
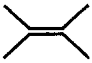
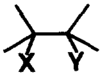
We wish to report that (a) a large number of olefin adducts of phenylselenenyl chloride are both thermally and solvolytically stable, (b) most of the phenylselenenyl chloride/olefin adducts which are unstable at room temperature can be cleanly produced by carrying out the reactions at temperatures below -50°C, and (c) the olefin adducts are formed in high yield with high regiospecificity. Our results are summarized in Table I.

As noted previously by Raucher[3b], addition of phenylselenenyl chloride to terminal olefins initially produces anti-Markovnikov adducts which isomerize on standing to the thermodynamically more stable Markovnikov adduct (Entries 2 and 3). With styrene, however, only the Markovnikov adduct is observed (Entry 1).

Disubstituted olefins react quickly with phenylselenenyl chloride to yield the corresponding trans adducts (Entries 4, 5, 6, 8, and 9), as long as the double bond is not inductively or conjugatively deactivated (Entries 7 and 9). In Entry 9 addition of phenylselenenyl chloride initially generates endione 1 which slowly isomerizes to its aromatic analog. No addition to the conjugated double bond is observed, even in the presence of excess reagent.[4]

TABLE I

Entry	Substrate	Product[a] (X=Cl, Y=SePh)	Solvent[b]/ Temp(°C)	Time[c]	Yield(%)[d]
1			CD_3CN/25	i	100
2			CCl_4/-10	i	94[e]
3			CD_3CN/25	24 hrs.	100
4			CD_3CN/25	i	100
5			CD_3CN/25	i	100
6			$CDCl_3$/25	i	100
7		----	$CDCl_3$/55	8 hrs	N.R.
8			CD_3CN/25	i	95
9			CD_3CN/25	30 min	100

Entry	Substrate	Product[a] (X=Cl, Y=SePh)	Solvent[b] Temp(°C)	Time[c]	Yield(%)[d]
10		----	$CDCl_3$/25	6 hrs	N.R.
11			$CDCl_3$/25	i	96[e]
12			$CDCl_3$/-50	i	100
13			$CDCl_3$/-50	i	100
14			$CDCl_3$/-50	i	100
15			$CDCl_3$/-50	i	100

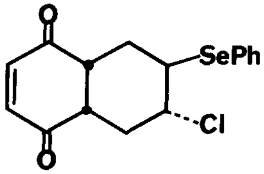
a) All reactions were carried out in an nmr tube using 1 equiv of PhSeCl and 1 equiv of reactant. Products were identified by analysis of their ir and nmr spectra. The mass spectra of all stable compounds were also determined and found to be consistent with the assigned structure.

b) In general, $CDCl_3$ or CD_3CN could be used interchangeably.

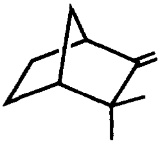
c) i = instantaneous.

d) Yields were determined spectroscopically. Isolated yields did not differ significantly from spectroscopically-determined yields. N. R. = no reaction.

e) The remainder of the product was the other regioisomer.



1



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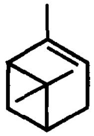

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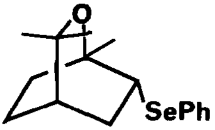

4

With the exception of 1-methylcyclohexene (Entry 11), all the adducts of tri- and tetra- substituted double bonds shown in Table I are to varying extents unstable at room temperature. However, if the reactions are done at temperatures below -50°C, the Markovnikov adducts are clearly produced (Entries 12, 13, 14, and 15). Unlike terminal olefins, no kinetically-formed anti-Markovnikov adducts are observed. Systems which are prone to Wagner-Meerwein rearrangements (e.g., 2 and 3) yield complex mixtures, regardless of the reaction temperatures employed.

Finally, it is interesting to note that terpineol (Entry 13) does not spontaneously cyclize to 4 but instead forms the phenylselenenyl chloride adduct. Cyclization to cineol derivative 4 can be achieved in 90% yield if the reaction is carried out in methylene chloride at -78°C in the presence of triethylamine.[6,7]

References:

1. We wish to thank the Petroleum Research Fund, administered by the American Chemical Society, and Research Corporation for financial support. We also thank the National Science Foundation for funds for the purchase of our Finnegan 4000 GC-MS system.

2. (a) K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, 34, 429 (1974); (b) H. J. Reich, *J. Org. Chem.*, 34, 428 (1974); (c) D. L. J. Clive, *Chem. Commun.*, 100 (1974).

3. (a) E. G. Kataev, T. G. Mannafov, E. A. Berdnikov and O. A. Komarovskaya, *Zhur. Org. Khim.*, 9, 1983 (1973); (b) S. Raucher, *J. Org. Chem.*, 42, 2950 (1977).

4. Entry 10 fails to undergo any detectable reaction after six hours at room temperature.

5. Virtually all the "stable" phenylselenenyl chloride/olefin adducts exhibit detectable amounts of decompositon approximately one day after being isolated.

6. K. C. Nicolaou and Z. Lysenko, *Tetrahedron Lett.*, 1257 (1977).

7. D. L. J. Clive, G. Chittattu, N. Curtis, W. Kiel and C. K. Wong, *J. Chem. Soc., Chem. Comm.*, 725 (1977).

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