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PHENYLSELENIUM AZIDE ADDITION TO ALKENES. A NEW AND STEREOSPECIFIC INTRODUCTION OF Se AND N INTO ORGANIC MOLECULES.[1]

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Abstract: The first examples of direct introduction of PhSe and N_3 functions by addition to olefins are reported. The addition of $PhSeN_3$ to simple alkenes, as well as to activated alkenes takes place in the absence of a catalyst. The reaction proceeds stereospecifically but not regiospecifically, apparently via a 3-membered selenonium ion intermediate.

In recent years phenylselenium derivatives have shown considerable utility in organic synthesis.[2] PhSeBr and PhSeCl behave as electrophiles toward olefins and in the presence of carboxylic acids or their silver salts lead to a useful synthesis of allyl alcohols.[2a-c] Uemura et al[3] and Tomada and coworkers[4] showed that PhSeCN is also capable of addition to olefins but that this generally requires the presence of Lewis acid catalysts. A mixture of PhSeCl and silver nitrite has been used to nitroselenate alkenes.[5] We report here the first examples of addition of $PhSeN_3$ to simple as well as to activated olefins without the need of a catalyst.

Thus cyclohexene reacted with a PhSeCl-NaN_3 mixture in DMSO at room temperature to produce stereospecifically the trans $PhSeN_3$ adduct 1 isolated in 91% yield. The presence of the azide function was obvious from the strong IR-band at 2100 cm^{-1}. The trans stereochemistry in 1 was indicated by two similar doublets of doublets of doublets with coupling constants of 10, 10 and 4 Hz indicative of equatorial substituents at C-1 and C-2.[6] The correlated ^{13}C spectra indicate the CH-Se absorption at 46.9 ppm with the corresponding H absorbing at 3.04 ppm, while the CH-N_3 absorbed at 64.38 ppm and the H at 3.29 ppm. In a similar manner 2 and 5 were formed from cyclooctene and dihydropyran respectively.

In order to establish whether it is $PhSeN_3$ that adds to the double bond or whether PhSeCl addition takes place followed by reaction with azide ions we treated PhSeCl with an insoluble azidation polymer[7] and reacted the resulting solution, after filtration, with cyclohexene. The formation of 1 speaks for a $PhSeN_3$ reagent. The above mentioned results as well as the clean formation of erythro and threo diastereomers 3 and 4 from trans and cis 2-butene respectively are compatible with the intermediacy of a 3-membered ring selenonium ion intermediate 13 formed during IN_3 additions[8] to olefins.

The electrophilic character of the Se portion of the reagent is further obvious from the strong activating and directive effect of an O or N substituent on the double bond. Thus enol ethers or enamines led regiospecifically to α-azido ethers or amines (see 5, 6 and 10).[6] On the other hand, no $PhSeN_3$ addition to ethyl crotonate was observed, indicating the deactivating influence of a carboethoxy group.

Terminal olefins such as 1-hexene, styrene or isobutylene gave $PhSeN_3$ adducts, but unlike in the case of ionic IN_3 additions[8], a mixture of regioisomers (see 7,8 or 9a and b) was obtained.[6] The regiochemical results are indicative of a 3-membered ring intermediate 12, in which most of the charge resides on Se (except in the case of substituents such as O or N which can more readily stabilize a positive charge in the transition state). Opening of 12 by azide ion occurs with almost equal facility at each carbon; terminal attack competing effectively even in styrene, possibly due to steric reasons. By contrast, in an iodonium intermediate 12, the ring carbons assume a great deal of positive character; thus, IN_3 addition to 1-hexene, isobutylene or styrene gives only one regioisomeric product (an analog of 7a, 8a or 9a respectively). The apparent 1,4-addition of $PhSeN_3$ to cyclohexadiene (see 11) is probably the result of 1,2-addition followed by rearrangement of the allylic azide.

A typical procedure involves stirring a mixture of 0.001 mole of PhSeCl with 0.001-0.002 mole of NaN_3 and 0.001 mole of cyclohexene in 5 ml of dry DMSO at room temperature overnight. After that period, 20 ml of t-BuOMe was added and the solution was washed well with water and evaporated to give trans 1-phenylseleno-2-azidocyclohexane 1 in 91% yield. No starting cyclohexene or other isomeric products were detected by nmr. Sodium periodate oxidation of 1 gave an isolable azido selenoxide which eliminated PhSeOH on heating in chloroform in the presence or absence of 1 equiv. of pyridine to produce a mixture of vinyl azide and allyl azide. Further studies to elucidate the scope and synthetic potential of these reactions are underway.

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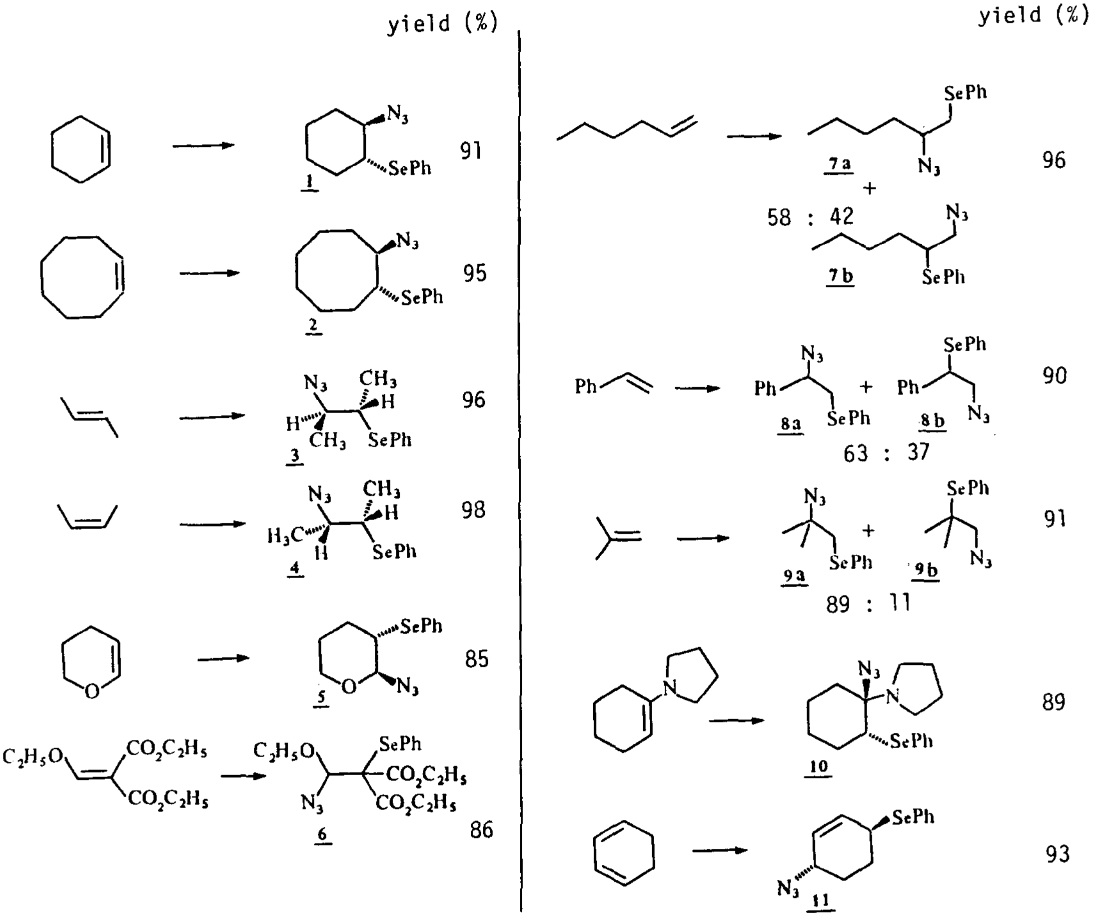
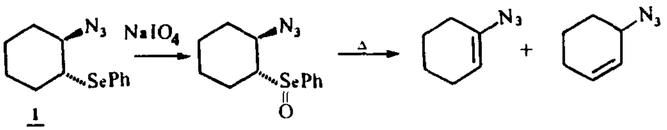

yield (%)
N3
SePh
1
91
N3
SePh
2
95
N3
CH3
H
H
CH3
SePh
3
96
N3
CH3
H
H3C
H
SePh
4
98
SePh
O
N3
5
85
C2H5O
CO2C2H5
CO2C2H5
C2H5O
SePh
CO2C2H5
N3
CO2C2H5
6
86
yield (%)
SePh
7a
N3
96
+
58 : 42
N3
7b
SePh
Ph
N3
Ph
8a
SePh
+
SePh
Ph
8b
N3
90
63 : 37
N3
9a
SePh
+
SePh
9b
N3
91
89 : 11
N
N3
N
10
SePh
89
SePh
N3
11
93


N3
SePh
1
NaIO4
N3
SePh
O
Δ
N3
+
N3

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