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SYNTHESIS OF CONJUGATED NITROALKENES VIA NITROSELENENYLATION OF ALKENES

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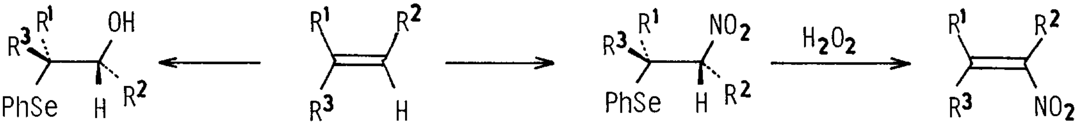
Summary: Addition of silver nitrite to 2-bromoalkyl phenyl selenide in the presence of mercury(II) chloride afforded 2-nitroalkyl phenyl selenide, which upon oxidative deselenenylation provided the conjugated nitroalkene in excellent yield.

The chemistry of aliphatic nitro compounds has recently received much resurgent attention because of their importance in organic synthesis.1) In particular, conjugated nitroalkenes are very useful synthetic intermediates.2) Although numerous procedures have appeared for the synthesis of conjugated nitroalkenes3), only a few employ the direct introduction of a nitro group into the carbon-carbon double bond.3a,b,4) The most promising of these is the Corey procedure which involves nitromercuration of alkenes.3a) We now describe a novel and stereospecific method which is applicable to both cyclic and acyclic alkenes.

The new method is based on nitroselenenylation of alkenes. Despite many examples of 1,2-addition reactions of organoselenium reagents across carbon-carbon double bond5), nitroselenenylation has been hitherto unexplored methodology to introduce a nitro group in alkenes (1). Initial attempts using benzeneselenenyl bromide and silver nitrite resulted in a mixture of 2-nitroalkyl phenyl selenides (2) and 2-hydroxyalkyl phenyl selenides (3) with the latter being predominant (Eq. 1)6). The disappointing results were at first attributed to ambident character of nitrite anion. However, after thorough screening studies of catalysts, it was found that the formation of 3 could be significantly or in some cases completely suppressed if the reactions were conducted in the presence of mercury(II) chloride.



(3) (1) (2) (4) (1)

Table 1 lists the yields of 2 and 3. Structures of these compounds were identified by IR, ^{1}H- and ^{13}C-NMR spectra and elemental analysis. As seen from the Table, the formation of by-product 3 was minimized under these conditions and in some cases (1a, 1b, 1f, 1h and 1i) completely eliminated. It was shown that each symmetrical alkene (1a-1e) afforded a single stereoisomer of the nitro compound (2) within the limits of ^{13}C-NMR detection, suggesting that the reactions are stereoselective. Trans-relationship between the phenylseleno and nitro groups was strongly suggested in the case of cyclohexene (1b) by a large coupling constant (J= 10.8 Hz) between H-1 and H-2. That the reaction is also stereospecific was unequivocally established by

Table 1. Nitroselenenylation of alkenes[a]

Compd. number suffix	Alkenes (1)	Yields (%)[b] 2	3
a	Cyclopentene	70	0
b	Cyclohexene	81	0
c	Cycloheptene	76	6
d	(E)-4-Octene	66	21
e	(Z)-4-Octene	77	12
f	(Z)-2-Pentene	72[c]	0
g	1-Hexene	75[d]	10
h	Styrene	83[e]	0
i	3-Cyclohexene-carbaldehyde	58[f]	0

[a] Reactions were run in acetonitrile-tetrahydrofuran mixture at -78°C to 22°C under argon using the molar ratio of the reagents; PhSeBr:alkene:$HgCl_2$:$AgNO_2$ = 1.0 : 1.0 : 1.3 : 1.0. [b] Isolated yield after silica-gel chromatography. [c] 1-Ethyl-2-nitropropyl phenyl selenide : 1-methyl-2-nitrobutyl phenyl selenide = 64 : 36 (by ^{1}H-NMR). [d] 2-Nitrohexyl phenyl selenide : 1-nitromethylpentyl phenyl selenide = 78 : 22 (by ^{1}H-NMR). [e] Only β-nitrophenethyl phenyl selenide was obtained. [f] Obtained as an inseparable regioisomer mixture.

using (E)- and (Z)-4-octenes (1d and 1e); the ^{13}C-NMR spectra of 2-nitroalkyl phenyl selenides (2d and 2e), each obtained as a single stereoisomer, were clearly different. As expected, unsymmetrical alkenes (1f, 1g and 1i) provided regioisomeric mixtures. Thus, 1-hexene gave Markownikow product and anti-Markownikow product in the ratio 78 : 22. On the other hand, styrene (1h) provided the regiospecific product in which the phenylseleno group was introduced at the terminal carbon atom.

The nitro selenides (2) thus obtained were easily oxidized with hydrogen peroxide to afford conjugated nitroalkenes 4 in high yields (Eq. 1) in a completely stereospecific manner; the ^{1}H-NMR spectra of the nitroalkenes 4d and 4e, derived from the diastereomers 2d and 2e, respectively, were clearly different.6) Although the overall yield of nitroalkenes (4) from alkenes (1) is slightly lower than nitromercuration (~80%)[3a], the advantage of our procedure over nitromercuration is avoidance of aqueous medium, which allows application to virtually any alkenes which may be insoluble in water. Further studies are now in progress.

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