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SYNTHESIS OF 2-NITROALKYL PHENYL SELENIDES AND THEIR CONVERSION TO NITROALKENES

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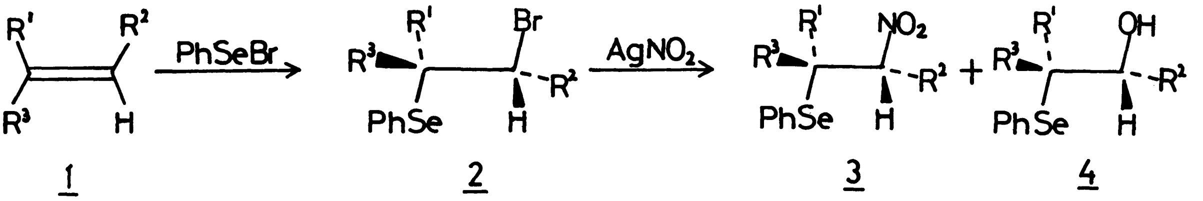
Treatment of alkenes with benzeneselenenyl bromide followed by addition of silver nitrite provided a mixture of 2-nitroalkyl and 2-hydroxyalkyl phenyl selenides. Oxidation of the former selenides with hydrogen peroxide gave nitroalkenes in 90–93% yields.

Conjugated nitroalkenes are very useful synthetic intermediates[1)] and various new approaches have been reported recently. These involve nitromercuration of olefins,[1b)] nitrodestannylation,[2)] reduction-elimination sequence on α-nitro ketones,[3)] oxidation-elimination sequence on α-halo ketoximes,[4)] and oxidative elimination of 1-nitroalkyl phenyl selenides.[5)] Herein we wish to report a novel method for the preparation of conjugated nitroalkenes from simple alkenes (1) via 2-nitroalkyl phenyl selenides.

The new method is based on the electrophilic addition of organoselenium reagents across carbon-carbon double bond. It is known that 2-bromoalkyl phenyl selenides (2), readily prepared from benzeneselenenyl bromide and alkenes, react with various nucleophiles such as water,[6)] alcohols,[7)] carboxylic acids,[8)] amines,[9)] and azides[10)] to provide the corresponding 2-substituted alkyl phenyl selenides in a highly stereospecific manner. No report, however, has yet appeared on the synthesis of 2-nitroalkyl phenyl selenide (3) using nitrite anion as a nucleophile. We have now found that 2 reacts with silver nitrite to give 3 and 2-hydroxyalkyl phenyl selenide (4) in 24–32% and 39–57% yields, respectively (Eq. 1).

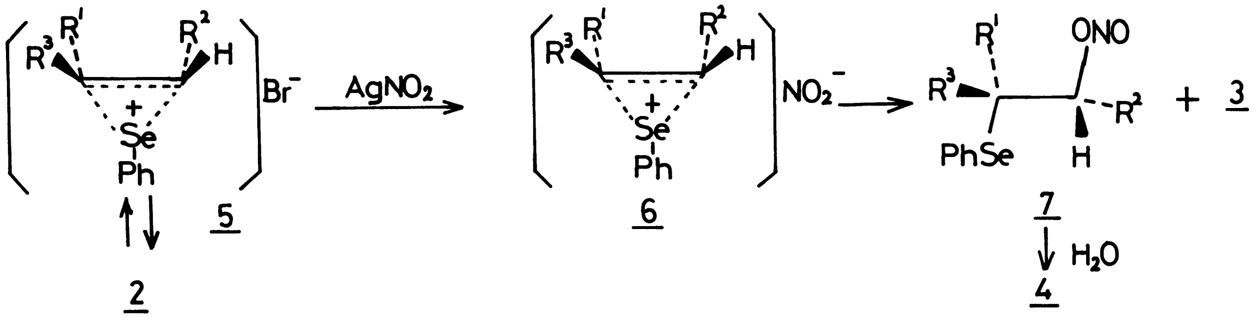


A typical procedure is as follows: Cyclohexene (1b, 164 mg, 203 μl, 2.0 mmol) was added to a magnetically stirred solution of benzeneselenenyl bromide (472 mg, 2.0 mmol) in dry dichloromethane (5.0 ml) at ambient temperature under argon. A solution of silver nitrite (307 mg, 2.0 mmol) in dry acetonitrile (5.0 ml) was then added to the reaction mixture which immediately deposited precipitates of silver bromide. After stirring for 1 h, the reaction mixture was filtered to remove the precipitates, which were washed thoroughly with dichloromethane. The filtrate and washings were combined and concentrated on a rotary evaporator. The residue was purified by dry column chromatography (Woelm silica, TSC) eluting with a hexane-dichloromethane mixture (2:1) to afford 1-nitro-2-phenylselenocyclohexane (3b, colorless oil, 32% yield) and 2-phenylselenocyclohexanol (4b, colorless oil, 41% yield). The reactions using other olefins were performed in an analogous manner.

Table 1 lists the pertinent data of 3 and 4. Structures of these compounds were consistent with their IR, ^{1}H- and ^{13}C-NMR spectra.[11] A salient feature of this nitroselenenylation reaction leading to 3 is the observation that each reaction in Table 1 afforded a single stereoisomer of 3. Thus, the 1-nitro-2-phenylselenocyclohexane (3b) from cyclohexene (1b) was obtained as a single stereoisomer in which the nitro and phenylseleno groups exist in *trans* configuration as shown by a large coupling constant between H-1 and H-2 (J=10.8 Hz). It is therefore suggested that nitroselenenylation may proceed via completely stereoselective *anti*-addition across carbon-carbon double bond. That the reaction is also stereospecific was unequivocally demonstrated by the reactions of *trans*- and *cis*-4-octenes; the respective 2-nitroalkyl selenide 3d and 3e, each obtained as a single stereoisomer, were clearly different from each other as shown by their ^{13}C-NMR spectra.

The mechanism shown in Scheme 1 may account for both stereoselectivity and stereospecificity of the reaction leading to 3.

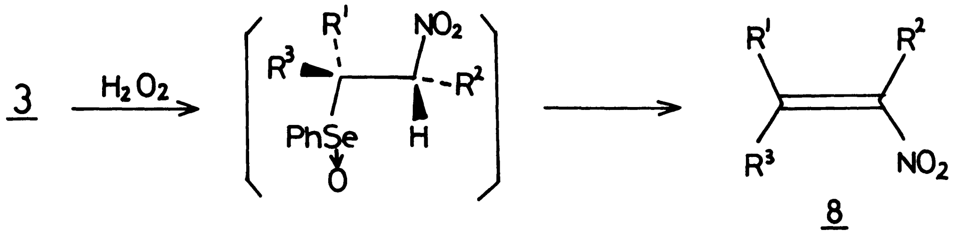
Scheme 1. Nitroselenenylation of alkenes



The 2-bromoalkyl selenide (2) is in equilibrium with seleniranium bromide 5 in solution. Upon addition of silver nitrite to 2, seleniranium nitrite 6 may be produced with concomitant precipitation of insoluble silver bromide. Nucleophilic attack of NO$_2^-$, an ambident nucleophile, at seleniranium cation from the less hindered side would produce 3 and nitrite ester 7. The latter would be rapidly hydrolyzed into 4 upon aqueous workup.

The nitro selenides 3 thus obtained were easily oxidized with hydrogen peroxide to give conjugated nitroalkenes 8 in high yield (Eq.2, Table 2): To a solution of nitro selenide (3d, 344 mg, 1.1 mmol) in dichloromethane (5.0 ml), 30% aqueous hydrogen peroxide (220 μl) was added at room temperature and stirred for

30 min. The mixture was dissolved in more dichloromethane and washed with 10% aqueous sodium carbonate. The solvent was removed in vacuo to give nitroalkene (8d, colorless oil, 158 mg, 92% yield).



(2)

Table 1 Yields and Spectral Data of 2-Nitroalkyl Phenyl Selenides (3) and 2-Hydroxyalkyl Phenyl Senenides (4)

Alkenes 1	Compd. number suffix	3		4	
		Yield[a] (%)	IR NO_2 (ν,cm^{-1})[b]	Yield[a] (%)	IR OH (ν,cm^{-1})[b]
Cyclopentene	a	24	1545, 1365	57	3400
Cyclohexene	b	32	1545, 1370	41	3420
Cycloheptene	c	30	1550, 1365	55	3440
trans-4-Octene	d	29	1550, 1360	42	3440
cis-4-Octene	e	24	1550, 1360	39	3420

[a] Isolated yield. [b] Measured as a neat liquid.

Table 2 Synthesis and Spectral Data of Nitroalkenes (8)

Nitro selenides 3	8	R^1	R^2	R^3	Yield[a] (%)	IR NO_2(ν,cm^{-1})[b]	^{1}H-NMR ($CDCl_3$) Olefinic proton (δ)
3a	8a	$-(CH_2)_3-$		H	91	1515, 1335	6.97-7.07(1H,m)
3b	8b	$-(CH_2)_4-$		H	93	1510, 1335	7.27-7.41(1H,m)
3c	8c	$-(CH_2)_5-$		H	92	1515, 1325	7.47(1H,t,J=6.9 Hz)
3d	8d	H	C_3H_7	C_3H_7	92	1520, 1345	5.67(1H,t,J=7.5 Hz)
3e	8e	C_3H_7	C_3H_7	H	90	1520, 1335	7.11(1H,t,J=7.8 Hz)

[a] Isolated yield from 3. [b] Measured as a neat liquid.

Again syn-elimination of benzeneselenenic acid from the selenoxide proceeded in a highly stereospecific manner: ^{1}H-NMR of nitroalkenes 8d and 8e, obtained from the diastereomers 3d and 3e, respectively, were clearly different.

Although the overall yields of nitroalkenes 8 from olefins are by no means excellent, the method reported herein may be significant in that the sequence involves two simple steps both of which are completely stereospecific. We are currently trying to find the conditions which minimize the formation of 4.

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