

Preparation of Nitroalkenes from the Corresponding Nitroalkanes

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Summary Phenylselenenyl bromide reacts with nitroalkanes to give nitro(phenylseleno)alkanes and oxidative elimination provided nitroalkenes.

In general, nitroalkenes, unique and versatile intermediates in synthetic work, are prepared by nitroalkane condensation or by the reaction of alkenes with nitrosyl halides or dinitrogen tetraoxide.^{1,2} In connection with our studies on nitro-

compounds, we required a general process oxidatively to transform a nitroalkane into its corresponding nitroalkene. This communication describes an efficient, one pot procedure for effecting this oxidation.

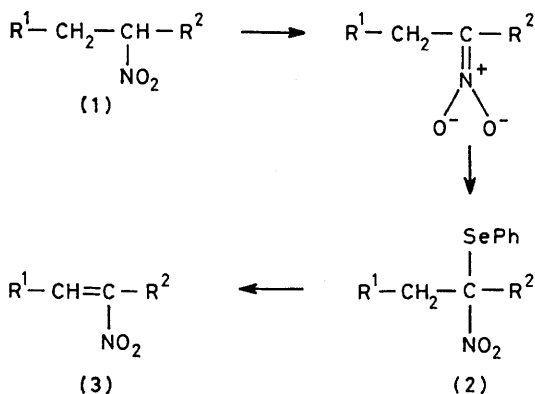
The results for a number of nitroalkane substrates are shown in the Table. Phenylselenenylation occurred smoothly when a solution of phenylselenenyl bromide (2:1 equiv.)† in anhydrous tetrahydrofuran (THF) was added

† When equimolar amounts of phenylselenenyl bromide and butyl-lithium were used, the yields of the nitroalkene were considerably reduced.

TABLE. Conversion of nitroalkanes into nitroalkenes.

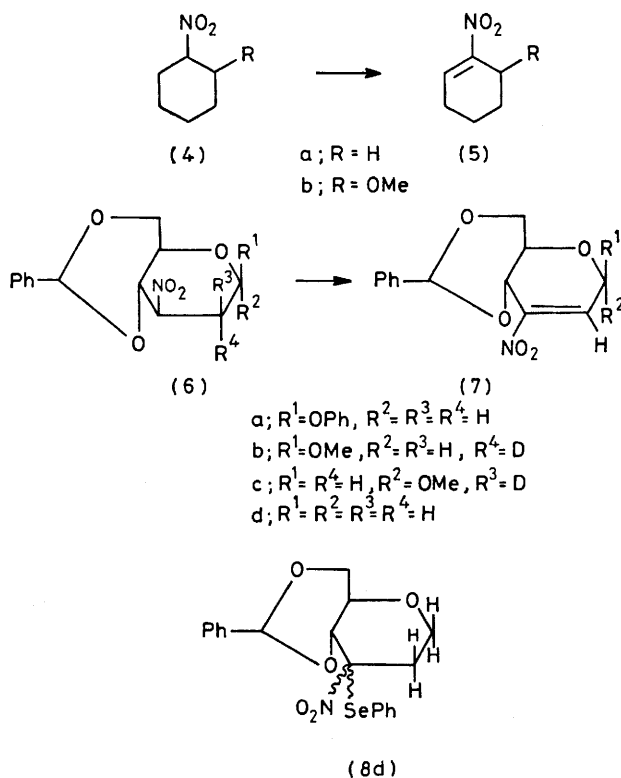
Nitroalkane	Selenide	Nitroalkene	% Yield ^a
(1a)	(2a)(61) ^b	(3a)	80(54)
(1b)		(3b)	83
(4a)		(5a)	55
(4b)		(5b)	61
(6a)		(7a)	80
(6b)		(7b)	75
(6c)		(7c)	67 ^c
(6d)	(8d)(61) ^b	(7d)	71(57)

^a Isolated overall yield from (1) by the one pot procedure; the figures in parentheses show the overall yield when the selenide was isolated. ^b Isolated yield. ^c Starting material was recovered in 11% yield.



a; R¹ = C₆H₁₃, R² = H

b; R¹ = C₇H₁₅, R² = H



(at 0 °C under N₂) to a solution prepared *in situ* by the addition of butyl-lithium (2 equiv.) to a nitroalkane in THF. Addition of 35% aqueous H₂O₂ caused oxidative elimination of the selenides to the desired 1-nitroalkenes regioselectively and in high yield, and, as expected for (4b),³ gave the allyl not the vinyl ether derivatives.

Since the selenides, especially those derived from 1-nitro-octane and 1-nitrononane, were found to decompose partially during isolation by silica gel column chromatography, the hydrogen peroxide was added directly to a THF solution of each selenide, thus improving the yield of the nitroalkene.

1-Methoxy-2-nitrocyclohexane (4b), prepared by the addition of methanol to 1-nitrocyclohexane, was converted into 3-methoxy-2-nitrocyclohex-1-ene, suggesting that the

present procedure has potential utility for the replacement of hydrogen atom(s) at the β and /or β' position by nucleophile(s). Furthermore this method provides stereochemical information about electrophilic addition to an aci-nitronate since disappearance of the deuterium atom during transformation of (6b)⁴ and (6c)⁷ into (7b)⁵ and (7c)⁶ indicated that the phenylselenenyl group approached from the α(axial position) and β(equatorial position) side of the molecule, respectively, the *cis* elimination being already established.⁸ Finally, the mild and non-basic conditions used for the final oxidative elimination mean that the present method provides a more convenient synthesis of the base-sensitive nitroalkene (7d)† from the nitroalkane (6d)§.

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† Conventional methods (Schmidt-Rutz reaction of the acetate or treatment of the nitro-alcohol with methanesulphonyl chloride-triethylamine) for the preparation of (7d) are always accompanied by double bond migration in the initial product (7d) (ref. 4).

§ Derived in almost quantitative yield by treatment of 2-*o*-acetyl-1,5-anhydro-4,6-*o*-benzylidene-3-deoxy-3-nitro-D-glucitol with NaBH₄ in dimethyl sulphoxide.

¹ For a general review of the chemistry of the nitro-group, see (a) Houben-Weyl, 'Methoden der Organischen Chemie,' ed. E. Muller, Georg Thieme Verlag, Stuttgart, 1971, Band 10/1, pp. 1-462; (b) 'The Chemistry of Nitro and Nitroso Groups,' ed. H. Feuer, Interscience, New York, Part 1, 1964, Part 2, 1970.

² For recently developed synthetic methods for 1-nitroalkenes see E. J. Corey, and H. Estreicher, *J. Am. Chem. Soc.*, 1978, **100**, 6294; *Tetrahedron Lett.*, 1980, **21**, 1113.

³ E.g., P. D. Magnus, 'Comprehensive Organic Chemistry,' ed. D. N. Jones, Pergamon, Oxford, 1979, Vol. 3, Part 12.

⁴ T. Sakakibara, Y. Nomura, and R. Sudoh, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1642.

⁵ H. H. Baer and T. Neilson, *Can. J. Chem.*, 1965, **43**, 840.

⁶ H. H. Baer and F. Kienzle, *Can. J. Chem.*, 1967, **45**, 983.