Tetrahedron Letters No. 44, pp 3909 - 3912, 1977. Pergamon Press. Printed in Great Britain.

THE SYNTHESIS OF VINYL BROMIDES AND ALLYL BROMIDES FROM MONOSUBSTITUTED ALKENES.[1]

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(Received in USA 10 August 1977; received in UK for publication 20 September 1977)

The synthesis of a wide variety of unsaturated compounds is possible by the oxidation of alkyl phenylselenides to the corresponding selenoxides followed by elimination of phenylselenenic acid.[2]

Recently we developed a procedure for the reaction of monosubstituted alkenes 1 with phenylselenenyl bromide to regioselectively give either the Markownikoff adducts 2 under thermodynamically controlled conditions, or the anti-Markownikoff adducts 4 under kinetically controlled conditions.[3] This led us to examine the possibility of utilizing these adducts for the synthesis of vinyl bromides and allyl bromides. We now report that the transformations detailed in Scheme I and Scheme II are possible by simple and convenient procedures.

The reaction of alkenes 1 with PhSeBr in CH_3CN gave the Markownikoff adducts 2 regioselectively.[3] Ozonization of 2b in CCl_4 at -20 °C produced the corresponding selenoxide; however, preliminary attempts to effect elimination at 25 °C or in refluxing CCl_4 resulted in the formation of a mixture of 2b and 3b. This disproportionation, which involves the reduction of unreacted selenoxide to selenide by initially formed PhSeOH, can be prevented by the addition of excess diisopropylamine prior to refluxing.[4] The overall conversion of alkenes 1 to 2-bromo-1-alkenes 3 then proceeds in good yield.

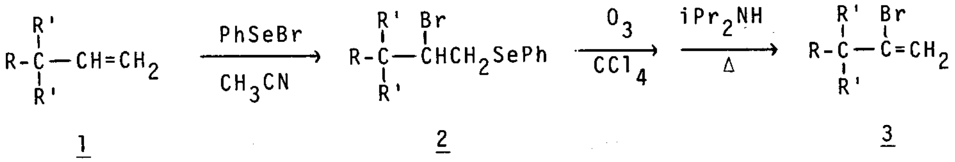
A typical experimental procedure for Scheme I follows:[5] a solution of 1-hexadecene (4.0 mmol) in CH_2Cl_2 (4 mL) was added to a solution of PhSeBr (4.0 mmol) in dry CH_3CN (20 mL) and stirred at 25 °C for 30 min. The solvents were removed in vacuo (25 °C), and the residue was dissolved in CCl_4 (40 mL) and ozonized at -20 °C until TLC showed disappearance of starting material. Diisopropylamine (20 mmol) was added and the resulting solution was refluxed for 30 min. Removal of solvents in vacuo and purification by filtration through silica gel (10 g) with hexane followed by evaporative distillation (140 °C, 0.005 mm) gave 2-bromo-1-hexadecene (1.02 g, 87%): ^1H NMR (CCl_4) δ 5.54 (m, 1H), 5.35 (d, J=0.5 Hz, 1H), 2.4 (m, 2H), 0.8-1.8 (m, 27H). IR (neat) ν 1625, 880 cm^{-1}.

The reaction of alkenes 1 with PhSeBr in CCl_4 gave the anti-Markownikoff adducts 4 regioselectively.[3] The best procedure for the oxidation-elimination for these adducts proved to be a two-phase oxidation with excess 30% H_2O_2 containing one equivalent of pyridine. The selenoxides derived from 4a-4f could conceivably undergo elimination to give either allyl bromides or vinyl bromides. In fact, adducts 4a-4c gave predominantly the allyl bromides 5a-5c with traces (<10%) of 1-bromo-1-alkenes indicated by NMR and VPC. Adduct 4d gave cinnamyl bromide (5d) exclusively. Adducts 4e and 4f failed to yield any characterizable products, presumably due to the lability of the expected allyl bromides. Finally, adducts 4g and 4h gave the vinyl bromides 6g and 6h as the E-isomer exclusively.

A typical experimental procedure for Scheme II follows:[5] a solution of 1-hexadecene (4.0 mmol) in CCl_4 (4 mL) was added to a solution of PhSeBr (4.0 mmol) in CCl_4 (10 mL) at 0 °C and stirred for 10 min. Pyridine (4 mmol) and 30% H_2O_2 (5 mL) was added and the reaction mixture was stirred vigorously at 0 °C for 30 min. The cooling bath was removed and stirring was continued for 3 hr. The CCl_4 layer was washed with water and dried ($MgSO_4$). Removal of solvents in vacuo and purification by filtration through silica gel (10 g) with hexane followed by evaporative distillation (160 °C, 0.005 mm) gave E-1-bromo-2-hexadecene (987 mg, 84%): ^1H NMR (CCl_4) δ 5.7 (m, 2H), 3.9 (m, 2H), 0.8-2.4 (m, 27H). IR (neat) ν 970 cm^{-1}.

The above procedures should prove useful for the synthesis of a variety of vinyl bromides and allyl bromides from monosubstituted alkenes.[6]

SCHEME I



SCHEME II

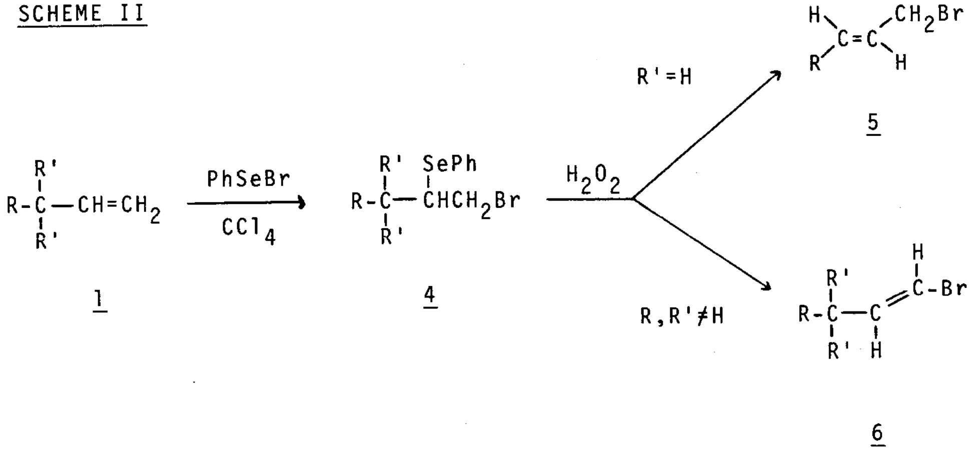


TABLE I Products and Yields for Scheme I and Scheme II.

Alkene	R	R'	SCHEME I		SCHEME II	
1a	nC_5H_{11}	H	3a	85%	5a	74%
1b	$nC_{13}H_{27}$	H	3b	87%	5b	87%
1c	$(CH_3)_2CH$	H	3c	67%	5c	67%
1d	C_6H_5	H	3d	75%	5d	79%
1e	H	CH_3	3e	70%		
1f	H	C_2H_5	3f	77%		
1g	CH_3	CH_3	3g	75%	6g	51%
1h	nC_4H_9	CH_3	3h	65%	6h	58%

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1. Organoselenium Chemistry 2. This research was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society. For previous paper see reference 3.

2. For a review see: (a) K. B. Sharpless, R. F. Lauer, D. W. Patrick, S. P. Singer and M. W. Young, *Chem. Scr.*, *8A*, 9 (1975); For synthesis of allylic alcohols, ethers, esters, and lactones see: (b) K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, *95*, 2697 (1973); (c) K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, *39*, 429 (1974); (d) H. J. Reich, *J. Org. Chem.*, *39*, 428 (1974); (e) H. J. Reich and S. K. Shah, *J. Am. Chem. Soc.*, *97*, 3250 (1975); (f) K. C. Nicolaou and Z. Lysenko, *J. Am. Chem. Soc.*, *99*, 3185 (1977); (g) K. C. Nicolaou and Z. Lysenko, *Tetrahedron Lett.*, 1257 (1977); For synthesis of α,β-unsaturated carbonyl compounds see: (h) H. J. Reich, I. L. Reich, and J. M. Renga, *J. Am. Chem. Soc.*, *95*, 5813 (1973); (i) H. J. Reich, J. M. Renga and I. L. Reich, *J. Org. Chem.*, *39*, 2133 (1974); (j) K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, *J. Am. Chem. Soc.*, *95*, 6137 (1973); (k) D.L.J. Clive, *J. Chem. Soc. Chem. Comm.*, 695 (1973); (l) D. N. Brattesani and C. H. Heathcock, Tetrahedron Lett., 2279 (1974); (m) P. A. Grieco and M. Miyashita, *J. Org. Chem.*, *39*, 120 (1974); (n) H. J. Reich, J. M. Renga and I. L. Reich, *J. Am. Chem. Soc.*, *97*, 5434 (1975); For Synthesis of alkenes see: (o) D. N. Jones, D. Mundy and R. D. Whitehouse, *J. Chem. Soc. Chem. Comm.*, 86 (1970); (p) K. B. Sharpless, M. W. Young and R. F. Lauer, *Tetrahedron Lett.*, 1979 (1973); (q) R. H. Mitchell, *J. Chem. Soc. Chem. Comm.*, 990 (1974); (r) K. B. Sharpless and M. W. Young, *J. Org. Chem.*, *40*, 947 (1975).

3. S. Raucher, *J. Org. Chem.*, *42*, 2950 (1977).

4. This type of disproportionation has been observed previously. R. D. Clark and C. H. Heathcock, *J. Org. Chem.*, *41*, 1396 (1976) and references cited therein.

5. All compounds were fully characterized by spectroscopic methods. Additional data for ^{1}H NMR (CCl_4): *3d* δ 3.8 (s, 2H), 5.45 (s, 2H). *3e* δ 1.1 (d, J=7 Hz, 6H), 2.5 (m, 1H), 5.3 (d, J=0.5 Hz, 1H), 5.6 (m, 1H). *3g* δ 1.2 (s, 9H), 5.40 (d, J=2 Hz, 1H), 5.65 (d, J=2 Hz, 1H). *6g* δ 1.05 (s, 9H), 6.27 (d, J=14 Hz, 1H), 5.95 (d, J=14 Hz, 1H).

6. We have utilized PhSeCl for the synthesis of vinyl chlorides and allyl chlorides. For example, 1-hexadecene gave 2-chloro-1-hexadecene (90% yield) by a procedure analogous to Scheme I, except that complete isomerization to the Markownikoff adduct requires 24 hours in CH_3CN at 25 °C (See ref. 3); and E-1-chloro-2-hexadecene (75% yield) by a procedure analogous to Scheme II.