# Reversal of the Phenylseleno- and Phenylsulpheno-cyclizations. Synthesis of Olefins from Phenylseleno- and Phenylsulpheno-lactones, Phenylselenoethers, and α-Hydroxyselenides

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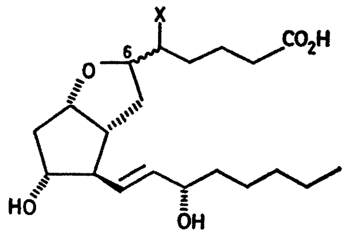
*Summary* Sodium in liquid ammonia reacts with phenylseleno- and phenylsulpheno-lactones, phenylselenoethers, and α-silyloxyselenides to give olefinic products in good to excellent yields.

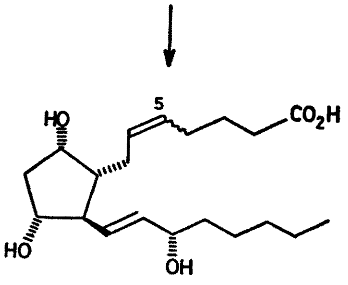
We[1,2] and others[3] have recently described several organoselenium- and organosulphur-induced ring closures and demonstrated their usefulness in synthesizing complex, biologically active molecules in the prostacyclin series.[1b,4]

We here report on the reversal of this general cyclization reaction which should enhance even further the usefulness of this method in organic synthesis.

While tri-n-butyltin hydride in the presence of a radical initiator removes reductively the phenylseleno-group from the prostanoid phenylseleno-ether (**1**) (mixture of diastereoisomers) to give 5,6-dihydroprostacyclin (**2**),[5] we found that Na–liquid $NH_3$ attacks the selenium and opens up the tetrahydrofuran ring to form $PGF_{2\alpha}$ (**3**)† together with its 5-*trans* isomer (**4**), (*cis*:*trans*, *ca.* 1:2·5)‡ in 75% total yield. Pure C-6 epimers gave similar results.



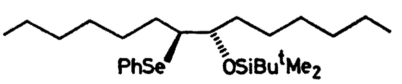
(1), X = SePh
(2), X = H



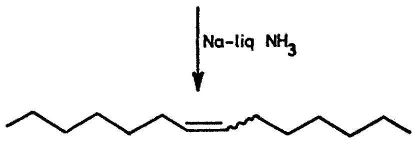
(3), 5-*cis*
(4), 5-*trans*

As the Table shows, this ring-opening reaction was found to be quite general for reversing the phenylseleno-etherification and the phenylseleno- and phenylsulpheno-lactonization reactions to form unsaturated products in good to excellent yields.

The procedure consists of adding an ethereal solution of the compound to excess of sodium dissolved in liquid ammonia at —78 °C, removing the cooling bath, and stirring for 5—10 min before quenching with solid ammonium chloride.

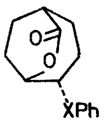
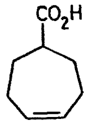
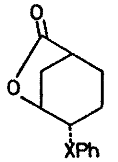
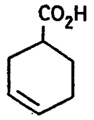
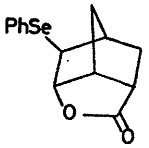
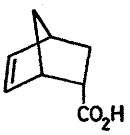
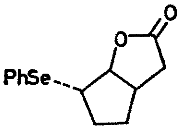
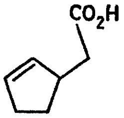
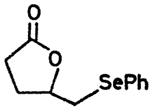
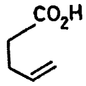
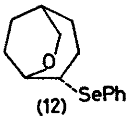
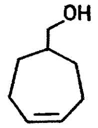
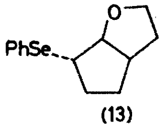
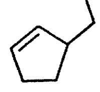


(14)



(15)

TABLE. Reversal of phenylseleno- and phenylsulpheno-cyclizations.

| Substrate | Product | % Yield |
|---|---|---|
| <br>(5) X = Se<br>(6) X = S |  | 82 (X = Se)<br>80 (X = S) |
| <br>(7) X = Se<br>(8) X = S |  | 77 (X = Se)<br>79 (X = S) |
| <br>(9) |  | 78 |
| <br>(10) |  | 80 |
| <br>(11) |  | 75 |
| <br>(12) |  | 78 |
| <br>(13) |  | 82 |

The present method could be extended to the preparation of olefins from α-hydroxyselenides[6] *via* their t-butyldimethylsilyl derivatives as exemplified by the formation of octadec-1-ene (78% yield) from the corresponding silyloxyselenide (mixture of regioisomers). However, whenever possible, mixtures of geometrical isomers are obtained with the *trans* isomer predominating as demonstrated by the conversion of (**14**) into (**15**) (75% yield; *cis*:*trans*, *ca.* 1:4).

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† All compounds exhibited satisfactory spectral data.

‡ The two isomers were separated as their tris(t-butyldimethylsilyl)ethers methyl esters on a silver nitrate impregnated silica column.

It is hoped that the described methodology together with the previously reported selenium- and sulphur-induced ring closures will find applications in selective protection–deprotection operations, as well as isomerizations of double bonds. This is clearly demonstrated by the transformations reported above in the prostaglandin series.

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[1] (a) K. C. Nicolaou and Z. Lysenko, *J. Amer. Chem. Soc.*, 1977, **99**, 3185; *Tetrahedron Letters*, 1977, 1257; (b) K. C. Nicolaou, W. E. Barnette, and R. L. Magolda, *J. Amer. Chem. Soc.*, 1978, **100**, 2567.

[2] K. C. Nicolaou and Z. Lysenko, *J.C.S. Chem. Comm.*, 1977, 293.

[3] D. L. J. Clive and G. Chittattu, *J.C.S. Chem. Comm.*, 1977, 484; D. L. J. Clive, G. Chittattu, N. J. Curtis, W. A. Kiel, and C. K. Wong, *ibid.*, 725; D. L. J. Clive, C. K. Wong, W. A. Kiel, and S. M. Menchen, *ibid.*, 1978, 379; D. L. J. Clive, G. Chittattu, and C. K. Wong, *Canad. J. Chem.*, 1977, **55**, 3894.

[4] K. C. Nicolaou and W. E. Barnette, *J.C.S. Chem. Comm.*, 1977, 331.

[5] K. C. Nicolaou, G. P. Gasic, and W. E. Barnette, *Angew. Chem. Internat. Edn.*, 1978, **17**, 293; E. J. Corey, H. L. Pearce, I. Szekely, and M. Ishigura, *Tetrahedron Letters*, 1978, 1023; see also D. L. J. Clive, G. Chittattu, and C. K. Wong, *J.C.S. Chem. Comm.*, 1978, 41.

[6] For alternative methods for this transformation, see: D. L. J. Clive, *Tetrahedron*, 1978, **34**, 1049 and references cited therein.