Tetrahedron Letters Vol. 21, pp 3827 - 3828
©Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/0922-3827\$02.00/0

ANODIC ACETAMIDOSELENATION OF ALKENES

Alan Bewick, David E. Coe, Geoffrey B. Fuller and John M. Mellor*
Department of Chemistry, The University, Southampton, SO9 5NH.

Summary: Anodic oxidation of diphenyldiselenide in acetonitrile in the presence of an alkene gives acetamidoselenides.

We have recently reported[1] the anodic oxidation of disulphides in acetonitrile in the prescence of alkenes to afford acetamidosulphides. This procedure permitting vicinal addition of nitrogen and sulphur substituents to an alkene has no simple non-electrochemical analogy. In contrast, many non-electrochemical procedures[2] permit electrophilic addition of sulphur and oxygen substituents to alkenes. The versatility of organoselenium intermediates in organic synthesis[3] has stimulated development of non-electrochemical methods[4] for vicinal addition of selenium and oxygen substituents to alkenes. Recently anodic oxidation of diphenyldiselenide has been used in an elegant synthesis of rose oxide[5] and to achieve vicinal addition[6] of selenium and oxygen substituents to alkenes. Neither electrochemical or non-electrochemical methods have been developed to permit vicinal addition of selenium and nitrogen substituents to alkenes directly. We now report such a transformation in the anodic acetamidoselenation of alkenes.

In acetonitrile, diphenyldiselenide gives a single irreversible oxidation wave ($E_{p/2}$ 0.96 V versus Ag/0.01 M Ag^+ reference electrode; sweep rate 0.1 V/s). On the reverse cathodic sweep, no reduction wave is observed. Under these conditions as with diphenyldisulphide[1] no evidence for an intermediate cation radical has been found. Preparative studies made in a three compartment cell, using a platinum foil anode, Bu_4NBF_4 as support electrolyte, and with passage of two coulomb equivalents of charge per mole of diselenide are reported in the Table. In a typical experiment diphenyldiselenide (298 mg) was oxidised at +1.30 V (versus Ag/0.01 M Ag^+ reference) in acetonitrile (20 ml) containing cyclohexene (405 mg). After electrolysis, the anolyte was quenched in water and extracted with ether to afford the crystalline trans 2-acetamido-1-phenylselenocyclohexane (217 mg). m.p. 153-155° (from acetone) m/e 297 and 295 (M^+), ν_{max} 3320, 1645 cm^{-1} δ ($CDCl_3$, 100 MHz). 0.90-2.30 (8H, m), 1.92(3H, s), 3.00(1H dt J11 and 4Hz), 3.80(1H, b), 5.45(1H, b), 7.18-7.65(5H, m).

Such a transformation affording readily a crystalline product in satisfactory yield indicates further uses for organoselenium intermediates in the synthesis of complex amines. In this respect we note the high regioselectivity in addition to terminal alkenes, and the high stereoselectivity leading to trans addition to the cyclic alkenes. Such selectivity is anticipated from the many studies of addition of phenylselenyl halides and related reagents.

We thank NRDC for financial support of this work, which is the subject of British Patent Applications Nos. 7920649 and 7920650.

Table

Anodic Acetamidoselenation of Alkenes with Diphenyldiselenide[a]

Alkene	Products[b]	Yield %[c]
Hex-1-ene	2-Acetamido-1-phenylselenohexane	64
Oct-1-ene	2-Acetamido-1-phenylseleno-octane	62
Dec-1-ene	2-Acetamido-1-phenylselenodecane	99
Dodec-1-ene	2-Acetamido-1-phenylselenododecane	91
Hept-3-ene	3-Acetamido-4-phenylselenoheptane	70[d]
	4-Acetamido-3-phenylselenoheptane	
Cyclopentene	Trans 2-acetamido-1-phenylseleno-cyclopentane	66
Cyclohexene	Trans-2-acetamido-1-phenylseleno-cyclohexane	77
Cyclooctene	Trans-2-acetamido-1-phenylseleno-cyclooctane	41

a. PhSeSePh was electrolysed at +1.30 V versus Ag|0.01 M Ag$^+$ reference electrode

b. Products identified by high resolution ms, ir and ^{1}H nmr analysis.

c. Yields of isolated products based on diphenyldiselenide consumed.

d. Ratio of isomers 50:50.

REFERENCES

1. A. Bewick, D.E. Coe, J.M. Mellor and D.J. Walton, J.C.S. Chem. Comm., 1980, 51.
2. B.M. Trost, M. Ochiai and P.G. McDougal, J. Amer. Chem. Soc., 1978, 100, 7103; K.C. Nicolau, S.P. Seitz, W.J. Sipio and J.F. Blount, ibid, 101, 3884.
3. D.L.J. Clive, Tetrahedron, 1978, 34, 1049; H.J. Reich, Accounts Chem. Res., 1979, 12, 22.
4. T. Hori and K.B. Sharpless, J. Org. Chem., 1978, 43, 1689; H.J. Reich, I.L. Reich and S. Wollowitz, J. Amer. Chem. Soc., 1978, 100, 5981; S. Uemura, A. Toshimitsu, T. Aoai and M. Okano, J.C.S. Chem. Comm., 1979, 610; S. Vemura, A. Toshimitsu, T. Aoai and M. Okano, Tetrahedron Letters, 1980, 1533.
5. S. Torii, K. Uneyama and M. Ono, Tetrahedron Letters, 1980, 2653.
6. S. Torii, K. Uneyama and M. Ono, Tetrahedron Letters, 1980, 2741.

(Received in UK 18 July 1980)