Tetrahedron Letters,Vol.30,No.11,pp 1417-1420,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

THE REACTION OF DIPHENYL DISELENIDE WITH PEROXYDISULPHATE IONS IN METHANOL A CONVENIENT PROCEDURE TO EFFECT THE METHOXYSELENENYLATION OF ALKENES

M.Tiecco,* L. Testaferri, M. Tingoli,* D. Chianelli, and D. Bartoli

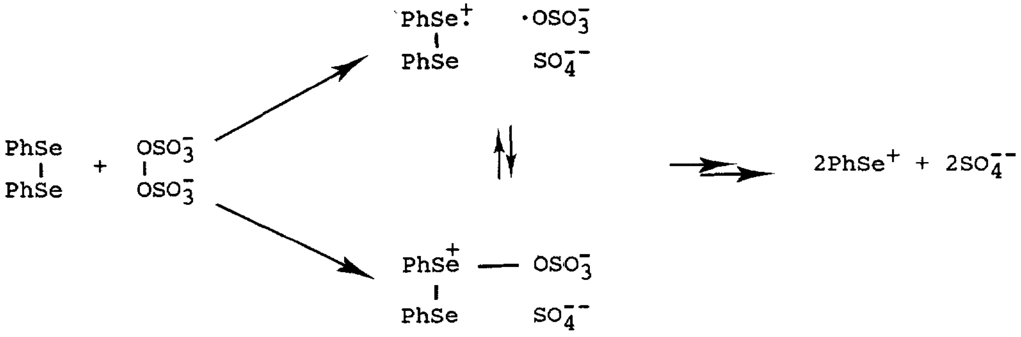
Istituto di Chimica Organica, Facolta' di Farmacia, Universita' di Perugia
06100 Perugia, Italy

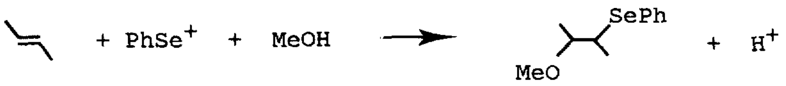
Abstract - Methoxyselenenylation of several alkenes was effected, in one step, by oxidation of diphenyl diselenide with ammonium peroxydisulphate in methanol.

The addition of phenylselenenyl chloride to an alkene, in the presence of alcohols, water, or acetic acid, usually results in solvent incorporation to afford the oxyselenenylation products.[1,2] The production of the electrophilic phenylselenium cation can also be effected by electrochemical oxidation of diphenyl diselenide, but this usually requires the use of halide anions as mediators.[3-5] However, the presence of the nucleophilic halide anions is sometimes responsible for some undesirable processes such as addition of the halide ion and decrease in stereoselectivity. Moreover, we have also recently observed that in several cases the addition of phenylselenenyl chloride to the alkenes is complicated by the fact that PhSeCl also reacts with the formed β -alkoxyalkyl phenyl selenides leading to deselenenylation products; the two processes often proceed with comparable rate and mixtures of products are thus obtained.[6,7] A reagent which is free from these complications seems to be the phenylselenenyl triflate, prepared from PhSeCl and CF_3SO_3Ag, which has been recently introduced to effect clean selenolactonization reactions[8] and cyclizations of olefinic alcohols.[9]

We describe herein a simple procedure to effect clean methoxyselenenylations of alkenes with several advantages over the previously described methods. This new procedure consists in the oxidation of diphenyl diselenide with peroxydisulphate ions in methanol.[10] This reaction, which can be suggested to initiate through an electron transfer or an S_N2 process,[11] produces phenylselenium cations in the absence of nucleophilic counter ions;

thus, in the presence of an alkene, the methoxyselenenylation products are smoothly formed. The results obtained are summarized in the Table.



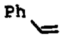
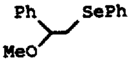
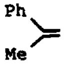
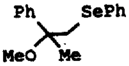
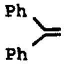
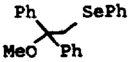
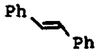
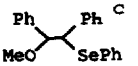
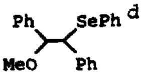
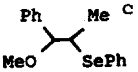
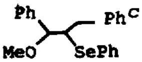
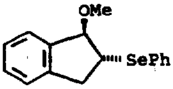
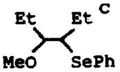
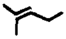
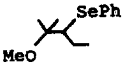
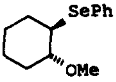
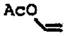
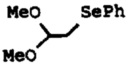
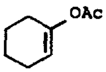
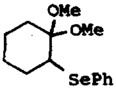
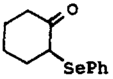


These reactions were carried out according to two general methods. A mixture of PhSeSePh (2.5 mmol) and $(NH_4)_2S_2O_8$ (3 mmol)^{12} in methanol (15 ml) was refluxed for 1-1.5h; after cooling, the alkene (5 mmol) was added and the resulting almost colourless mixture was stirred at room temperature for the time indicated in the Table (Method A). Under these conditions, with the less reactive alkenes some methoxydeselenenylation products were also formed.^{6,7} This could be avoided by allowing to react the $(NH_4)_2S_2O_8$ with an excess of PhSeSePh (7.5 mmol) in the presence of the alkene and at room temperature (Method B); this obviously required longer reaction times. After the usual work up of the reaction mixtures, the methoxyselenenylation products were obtained in a pure form by column chromatography on silica gel.^{13}

The oxidation of diphenyl diselenide can be effected with other oxidizing agents also. Thus, from the reaction of PhSeSePh with cerium ammonium nitrate, or potassium nitrate (with few drops of nitric acid),^{7} or with copper(II) sulphate in methanol, in the presence of styrene, the product of methoxyselenenylation was obtained in 92, 75 and 90% yield, respectively. However, when applied to other alkenes these procedures do not always give satisfactory results. Thus, ammonium peroxydisulphate seems to be the best oxidizing agent to perform these reactions.

The results collected in the Table show that good yields of the methoxyselenenylation products are obtained in every case indicating that this procedure has general applicability.^{14} With the alkenes employed for

TABLE

Run	Alkene	Method	Time(h)	Reaction Products	Yield(%)^{a}
1.		A	0.5		88
2.		A	0.5		95
3.		A	0.5		72^{b}
4.		B	15		79
5.		B	15		72
6.		B	15		68
7.		B	15		67
8.		B	15		89
9.		B	15		71
10.		A	0.5		78
11.		A	2		82
12.		A	1		86
13.		A	1	 and	32
					41

a) Calculated on isolated products. b) From the reaction carried out in CH_3CN/H_2O (5/1) the $Ph_2C(OH)CH_2SePh$ was obtained in 76% yield. c) Erythro. d) Threo.

the present investigation the reactions were completely regiospecific, the addition products being formed with Markovnikov orientation. Furthermore, the reactions proceed stereospecifically affording the products of anti addition.

On the basis of the present results the oxyselenenylation of alkenes [15] initiated by the peroxydisulphate anions oxidation of diphenyl diselenide can be considered a convenient alternative to known methods.

Acknowledgements. Financial support from the CNR, Rome, Progetto Strategico "Processi di Trasferimento Monoelettronico", and Ministero della Pubblica Istruzione, Italy, is gratefully acknowledged.

References and Notes

1) C. Paulmier, "Selenium Reagents and Intermediates in Organic Synthesis", Pergamon Press, Oxford, 1986.
2) D. Liotta, "Organoselenium Chemistry", Wiley Interscience, New York, 1987.
3) S. Torii, K. Uneyama, M. Ono, and T. Bannou, **J. Am. Chem. Soc.**, **103**, 4606 (1981).
4) K. Uneyama, M. Ono, and S. Torii, **Phosphorus Sulfur**, **16**, 35 (1983).
5) S. Torii, K. Uneyama, and M. Ono, **Tetrahedron Lett.**, 21, 2653, 2741 (1980).
6) M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, and D. Bartoli, **Tetrahedron**, **44**, 2261 (1988).
7) M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, and D. Bartoli, **Tetrahedron**, **44**, 2273 (1988).
8) S. Murata and T. Suzuki, **Chemistry Lett.**, 849 (1987).
9) S. Murata and T. Suzuki, **Tetrahedron Lett.**, **28** 4297, 4415 (1987).
10) This reaction can be carried out in other alcohols as well as in other solvents like CH_3CN or mixtures of CH_3CN and H_2O. In the latter case the products of hydroxyselenenylation are obtained.
11) The mechanistic aspects of this reaction are presently under investigation.
12) Larger excess of $(NH_4)_2S_2O_8$ should be avoided since it can react with the β-methoxyalkyl phenyl selenides to give different products depending on the structure of the starting alkenes. Unpublished results from this laboratory.
13) Products identification was carried out by comparison with authentic samples and by ^1H and ^{13}C nmr spectroscopy.
14) Intramolecular selenoetherification of olefinic alcohols and selenolactonization of olefinic acids can be easily carried out under conditions essentially identical to those described in this paper. Unpublished results from this laboratory.
15) This procedure can be also applied to alkynes and to enolizable ketones. In these cases however the reaction proceeds further to afford the product of alkoxydeselenenylation. This represents a convenient method to convert alkynes and methyl ketones into α-keto acetals. Unpublished results from this laboratory.

(Received in UK 24 January 1989)