Pergamon

Tetrahedron Letters, Vol. 35, No. 9, pp. 1449-1452, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(94)E0089-G

SELENOXIDE-SULFONIC ACID ADDUCTS; A NEW CLASS OF STABLE, SELENOXIDE-BASED OXIDANTS.

D. John Procter and Christopher M. Rayner*

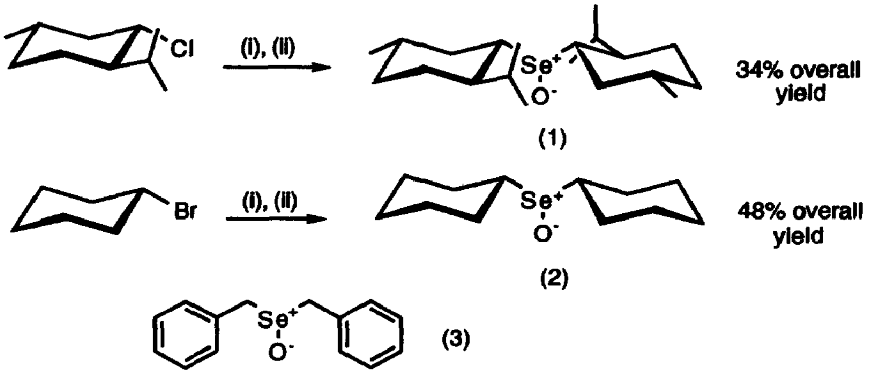
School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K..

Abstract: The preparation and characterisation of a novel class of adducts of selenoxides with sulfonic acids are described. They are considerably more stable and show superior reactivity to the parent selenoxides. Their structure has been confirmed by ^{1}H NMR spectroscopy and X-ray crystallography.

Organoselenium compounds have been used extensively in organic synthesis.[1] More recently, there have been an increasing number of reports of their use in asymmetric synthesis, for example in the preparation of enantiomerically enriched allylic alcohols *via* 2,3-sigmatropic rearrangements of allylic selenoxides[2], or allenes and alkenes by elimination of selenenic acid,[3,4] *via* enantiomerically enriched selenoxides produced either by asymmetric oxidation or chirality transfer. Chiral diselenides have also recently been reported as enantioselective selenylating agents.[5] We are interested in applications of new selenium based reagents in synthesis, and now wish to report a new class of selenium based oxidants which we believe will have widespread synthetic utility.

Since the original reports[1,6] of selenoxide based oxidations, relatively little work has followed, at least partly a result of the presumed instability of such species. Indeed, selenoxides are well known for their propensity for β-elimination reactions, a procedure which has been extensively exploited for the synthesis of unsaturated carbonyl compounds.[7] Dialkyl selenoxides are much less prone to such a reaction,[8] and many are isolable. An alternative mode of degradation for these compounds exists in which they can revert to the parent selenides over a period of hours. For example, dimenthyl selenoxide (1) reverts cleanly back to the selenide after approximately 12 hours at room temperature. We now wish to describe the formation of adducts between sulfonic acids and selenoxides, which are indefinitely stable at room temperature but still retain many of the properties we initially desired of selenoxides.

Dicyclohexyl selenoxide (2)[9], dibenzyl selenoxide (3)[6a] and dimenthyl selenoxide (1) were chosen as representative substrates and were synthesised as shown in scheme 1, either by the reported procedure or by the action of selenium oxychloride on Grignard reagents derived from cyclohexyl bromide and menthyl chloride.[10] Note that intermediate selenoxides produced in the Grignard reaction revert to the corresponding selenides under the reaction conditions, but can then be reoxidised efficiently (>90%).



Reagents: i) Mg, Et_2O; $SeOCl_2$ (0.4 eq.); ii) MCPBA (1.2 eq.), CH_2Cl_2, $NaHCO_3$, H_2O.

Scheme 1.

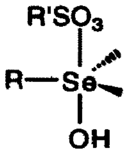
Dissolution of the selenoxides in deuterochloroform, followed by addition of an *anhydrous* sulfonic acid and observation by ^1H NMR shows clean formation of a different organoselenium species with considerable deshielding of protons on carbons adjacent to selenium atom (table 1). This is the case for a variety of sulfonic acids, including *p*-toluene-, *p*-bromobenzene-, trifluoromethyl- and 2,2,2-trifluoroethyl sulfonic acids. No similar adduct was formed with acetic acid. Removal of solvent, in most cases[11] leaves a colourless solid which can be recrystallised and fully characterised, a procedure which was not possible with the corresponding selenoxides. Selected physical data are shown in table 1.

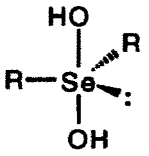
Entry	Selenoxide	Acid	^1H NMR[a]	M.P. (°C)
1	1	*p*-Toluene sulfonic	3.85, 3.40	b
2	1	*p*-Bromobenzene sulfonic	3.74, 3.35	b
3	1	$CF_3CH_2SO_3H$	3.84, 3.49	46.2-50.2
4	2	*p*-Toluene sulfonic	3.71	108.1-110.0
5	2	*p*-Bromobenzene sulfonic	3.68	96.1-98.4
6	2	$CF_3CH_2SO_3H$	3.89	80.6-83.3
7	3	*p*-Toluene sulfonic	4.66, 4.14	107.5-108.0
8	3	*p*-Bromobenzene sulfonic	4.63, 4.15	121.7-122.7
9	3	CF_3SO_3H	4.57, 4.12	c

Notes: [a] δ, $CDCl_3$, 25°C, resonances given are chemical shifts of protons α to selenoxide, corresponding values for parent selenoxides are (1) 2.93, 2.86, (2) 2.88, (3) 3.94, 3.99; [b] oil at room temperature; [c] see reference 11.

Table 1. Selected physical data of selenoxide-sulfonic acid adducts.

The actual structure of these new adducts is of particular interest. Importantly, the ^1H NMR spectra of the part of the adduct originally derived from the selenoxide, showed little variation between sulfonic acids (*cf.* entries 7 and 9). This, we believe, rules out the possibility of these adducts being any kind of selenurane[12] intermediate (4) when in solution, although a small equilibrium concentration cannot be ruled out. If such a selenurane were present then considerable variation of chemical shift of the protons α-to selenium would be expected, depending on the sulfonic acid used. The reactions were also performed under rigorously anhydrous conditions, so formation of the hydrate (5) was ruled out.[2,3,4] We believe a much more likely candidate is the salt like structure (6). The isolation and full characterisation of an such intermolecular complex is, to the best of our knowledge, the first of its kind, although compounds containing intramolecular hydrogen bonds between selenoxides and either hydroxyl or amide groups have been proposed.[13,14]


(4)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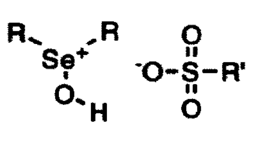
(6)

The remarkable stability of our adducts has allowed us to obtain an X-ray crystal structure of the adduct between *p*-bromobenzenesulfonic acid and dicyclohexyl selenoxide (7) (figure 1). Although this is, of course, the solid state structure of the adduct, it clearly shows protonation of the selenoxide oxygen, with a hydrogen bond to the sulfonate group, rather than any selenurane type structure.[15] There are relatively few X-ray crystal structures of selenoxides, mainly due to their instability, and the formation of these new adducts may be of considerable use in general selenoxide characterisation.[16]

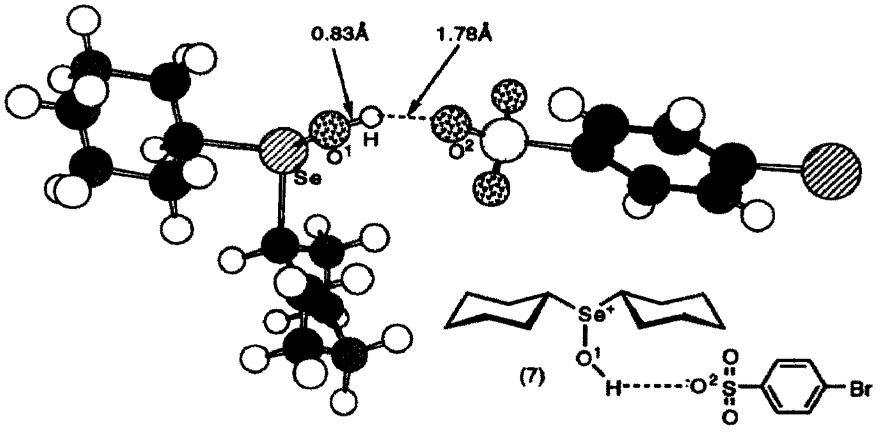

Figure 1.

Finally, these adducts retain many of properties we originally desired from selenoxides, and are superior in a number of ways. They are much more stable, with a good shelf-life, and are readily accessible.[17]

When dissolved in organic solvents they will cleanly oxidise dialkylsulfides to sulfoxides in excellent yield, with no overoxidation, and clean regeneration of selenide. For example, the adduct between 2,2,2-trifluoroethyl sulfonic acid and dimenthyl selenoxide (CH_2Cl_2, 25°C) will oxidise methyloctyl sulfide to the corresponding sulfoxide in 90% isolated yield.[18] This is a significant advance on previous selenoxide oxidations of sulfides, which inevitably required acetic acid as solvent, and is the first example of a homochiral selenoxide-based oxidant.[6] A more detailed account of this work will appear shortly.

In conclusion, we believe that the isolation and characterisation of these new, stable selenoxide adducts will greatly facilitate the use of selenoxides in synthesis, and we are currently investigating their properties further.

Acknowledgements: We wish to thank SERC for an earmarked studentship (DJP), the Nuffield Foundation for an award under its Scheme for Newly Appointed Science Lecturers (CMR), ICI Strategic Research Fund and the Royal Society for financial support. We also wish to thank Dr. Mark Thornton-Pett (University of Leeds) for the X-ray crystal structure determination.

References.

1. Paulmier, C. *Selenium Reagents in Organic Synthesis;* Pergamon Press, Oxford, **1986**.
2. Davis, F.A.; Billmers, J.M.; Stringer, O.D. *Tetrahedron Lett.*, **1983**, *24*, 3191; Davis, F.A.; Stringer, O.D.; McCauley, J.P. *Tetrahedron*, **1985**, *41*, 4757; Davis, F.A.; Reddy, R.T. *J. Org. Chem.*, **1992**, *57*, 2599.
3. Reich, H.J.; Yelm, K.E. *J. Org. Chem.*, **1991**, *56*, 5672.
4. Komatsu, N.; Murakami, T.; Nishibayashi, Y.; Sugita, T.; Uemura, S. *J. Org. Chem.*, **1993**, *58*, 3697 and references cited therein.
5. Deziel, R.; Goulet, S.; Grenier, L.; Bordeleau, J.; Bernier, J. *J. Org. Chem.*, **1993**, *58*, 3619; Fujita, K.I.; Iwaoka, M.; Tomoda, S.; *Chem. Lett.*, **1992**, 1123.
6. a) Barnard, D.; Woodbridge, D.T.; *Chem. Ind.*, **1959**, 1603; b) Ogura, F.; Yamaguchi, H.; Otsubo, T.; Tanaka, H. *Bull. Chem. Soc. Japan*, **1982**, *55*, 641.
7. Reich, H.J.; Renga, J.M.; Reich, I.L. *J. Amer. Chem. Soc.*, **1975**, *97*, 5434; for use in synthesis see Paquette, L.A.; Doherty, A.M.; Rayner, C.M. *J. Amer. Chem. Soc.*, **1992**, *114*, 3910 and references cited therein.
8. Sharpless, K.B.; Young, M.W.; Lauer, R.F. *Tetrahedron Lett.*, **1973**, 1979.
9. Arase, A.; Masuda, Y. *Chemistry Lett.*, **1975**, 419.
10. Arase, A.; Masuda, Y. *Chemistry Lett.*, **1975**, 1331; Strecker, W. *Berichte*, **1915**, *48*, 196.
11. Adducts with trifluoromethane sulfonic acid were too unstable for microanalysis, but could be clearly observed by ^1H NMR.
12. Okamoto, Y.; Chellappa, K.L.; Homsany, R. *J. Org. Chem.*, **1973**, *38*, 3172; Marino, J.P.; Larsen, R.D. *J. Amer. Chem. Soc.*, **1981**, *103*, 4642.
13. a) Toshimitsu, A.; Owada, H.; Aoai, T.; Uemura, S.; Okano, M. *J. Chem. Soc., Chem. Commun.*, **1981**, 546; b) Detty, M.R. *J. Org. Chem.*, **1980**, *45*, 274; c) An adduct between a selenoxide and chlorosulfonic acid has been proposed on the basis of conductivity measurements, see Paul, R.C.; Konwer, D.; Dhillon, D.S.; Puri, J.K. *J. Inorg. Nucl. Chem.*, **1979**, *41*, 55; d) Adducts of selenoxides with 2,2'-dihydroxy-1,1'-binaphthol have been reported, although no suggestions for their structure was given, see Toda, F.; Mori, K. *J. Chem. Soc., Chem. Commun.*, **1986**, 1357.
14. The enhanced stability of intramolecularly hydrogen bonded selenoxides has been noted, see reference 13a.
15. The original X-ray data was transferred into Chem3D Plus™ for display purposes.
16. Shimizu, T.; Kikuchi, K.; Ikemoto, I.; Kobayashi, M.; Kamigata, N. *J. Chem. Soc., Perkin Trans. 1*, **1989**, 597.
17. All new compounds were characterised by ^1H and ^{13}C NMR, IR, and mass spectra, and gave satisfactory elemental analysis and/or accurate mass spectra unless otherwise stated.
18. Only very low (<10%) enantiomeric excess has so far been observed.

(*Received in UK* 17 *November* 1993; *accepted* 7 *January* 1994)