Synthesis of Selenones: A Comparative Study

Alain Krief,*[a] Willy Dumont,[a] Jean-Noël Denis,[a] Guy Evrard,[b] and Bernadette Norberg[b]

[a] *Laboratoire de Chimie Organique, and*
[b] *Laboratoire de Chimie Moléculaire Structurale, Facultés Universitaires Notre-Dame de la Paix, 61, rue de Bruxelles, B-5000 Namur, Belgium*

The propensity of several reagents to oxidize selenides to selenones has been evaluated; the scope and limitations of the methods are presented.

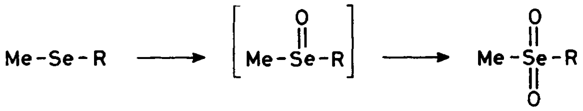
Although sulphones are very useful and widely used in organic synthesis, little is known about selenones.[1—3] A few papers, most of them belonging to the older literature, report the synthesis of diaryl,[4—8] aryl alkyl,[9,10] and dialkyl selenones.[11] They are however limited to very specific cases and many of them have been the subject of controversy.[9,11—13] More recently, selenones have been postulated as intermediates in valuable synthetic transformations[14—16] and some knowledge of their reactivity is of primary importance for the interpretation of the results.

We now report preliminary results of the synthesis of selenones by the oxidation of the corresponding selenides. This should involve the intermediary formation of a selenoxide (Table 1).

The oxidation of selenides to selenoxides and the ease with which these compounds produce alkenes, through selenenic acid elimination, is well documented[3,17—20] but overoxidation to selenones was not reported although in several instances an excess of oxidant was used.[3,17—20] This has led to the assumption[3] that the selenium atom in selenoxides is difficult to oxidize.

We have searched among various oxidants for those able to transform alkyl phenyl and dialkyl selenides to the corresponding selenones. Methyl phenyl and dimethyl selenides were first used as models since side reactions arising from the selenoxide elimination are not possible in these cases. 30% Hydrogen peroxide in tetrahydrofuran (THF), t-butylhydroperoxide in THF, and sodium periodate in ethanol[21] oxidized these selenides to selenoxides rapidly (at 20 °C) but were unable to produce the corresponding selenones even after prolonged reaction time. Ozone rapidly oxidizes both selenides to selenoxides at −50 °C, but whereas dimethyl selenoxide slowly produces (at 0 °C for 5 h) dimethyl selenone (32%) (Table 1), methyl phenyl selenoxide is not significantly

Table 1.

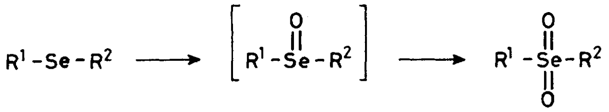


$$\text{Me-Se-R} \longrightarrow \left[\text{Me-}\overset{\text{O}}{\overset{\|}{\text{Se}}}\text{-R}\right] \longrightarrow \text{Me-}\underset{\underset{\text{O}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{Se}}}\text{-R}$$

Conditions	% Yield[a] R = Me (Time/h)	 R = Ph (Time/h)
O_3/CCl_4, 0 °C	32(5)[b,c,d,e]	traces (3)
2.5 mol. equiv. *m*-CPBA/CH_2Cl_2, 20 °C	85(1)	40 (2)
2.5 mol. equiv. CF_3CO_3H/CH_2Cl_2, 20 °C	—	70 (0.5)
1.5 mol. equiv. $KMnO_4/H_2O,CH_2Cl_2$, 20 °C	20(0.5)[b,c,d]	75 (0.5)
	5(5)[b,d]	18 (3)

[a] Unless otherwise stated the yields refer to pure isolated selenone. [b] These reactions have been monitored by ^{1}H and ^{77}Se n.m.r. spectroscopy. Yields are estimated by ^{1}H n.m.r. spectroscopy. [c] 'Oxidized seleninic acids' are present in the mixture: we are investigating the real structure of these compounds. [d] Selenoxide is present in the mixture. [e] We are unable to repeat on these examples the work of Paetzold (ref. 11). Moreover dibutyl selenoxide, prepared from the corresponding selenide dibromide, according to this author, also leads to the same mixture of compounds.

Table 2.



$$R^1\text{-Se-}R^2 \longrightarrow \left[R^1\text{-}\overset{\text{O}}{\overset{\|}{\text{Se}}}\text{-}R^2\right] \longrightarrow R^1\text{-}\underset{\underset{\text{O}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{Se}}}\text{-}R^2$$

Conditions	R^1	R^2	% Yield[a] (Time/h)
O_3/CCl_4, 0 °C	Bu^n	Bu^n	low[b,c,d,e] (6)
	Me	n-decyl	low[b,c,d,e] (6)
2.1 mol. equiv. *m*-CPBA/CH_2Cl_2, 20 °C	Me	Et	80 (2)
/$CHCl_3$	Me	n-decyl	71 (0.5)
/CH_2Cl_2	Me	2-tridecyl	—[b,c] (2)
/CH_2Cl_2	Bu	Bu	54 (15)
5 mol. equiv. *m*-CPBA/CH_2Cl_2, 20 °C	Ph	Et	14 (0.5)
	Ph	n-decyl	68 (5)
	Ph	2-decyl	—[b,c] (2)
2.5 mol. equiv. CF_3CO_3H/CH_2Cl_2, 20 °C	Ph	n-decyl	70 (0.3)
	Ph	n-decyl	76 (1)
1.5 mol. equiv. $KMnO_4/CH_2Cl_2$–H_2O, 20 °C	Me	Et	— (0.5)
	Me	Bu	50 (3)
	Me	n-decyl	87 (15)
	Me	2-tridecyl	91 (5)
	Bu	Bu	82 (15)
	Ph	Et	82 (0.5)
	Ph	n-decyl	low[b,d] (48)

[a—e] See footnotes a—e for Table 1.

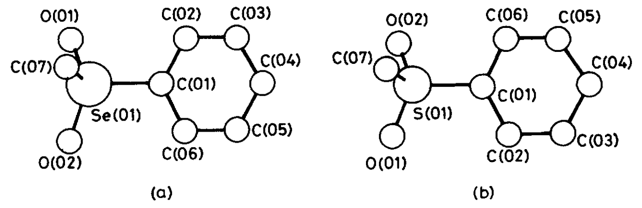


Figure 1. A comparison of bond lengths (Å) and angles (°) in (a) methyl phenyl selenone (X = Se) and (b) (in parentheses) methyl phenyl sulphone (X = S, ref. 22). X–C(01) 1.927(7) (1.832), X–O(01) 1.613(5) (1.453), X–O(02) 1.611(5) (1.465), X–C(07) 1.899(8) (1.761); C(01)–X–O(02) 108.4(3) (106.1), C(01)–X–C(07) 108.1(3) (112.6), C(01)–X–O(01) 107.7(3) (109.9), O(02)–X–C(07) 109.3(3) (107.7), O(02)–X–O(01) 115.2(3) (117.0), C(07)–X–O(01) 107.9(3) (103.8).

affected on further reaction with ozone[3] (an excess, 0 °C, 3 h). However, *m*-chloroperbenzoic acid (*m*-CPBA) and pertrifluoroacetic acid–phosphate buffer (2.5 equiv., 20 °C), were found efficient for the oxidation of both selenides to the corresponding selenones. Under these conditions, the formation of selenoxides is instantaneous whereas further oxidation to selenones occurs more slowly. Potassium permanganate proved valuable for the synthesis of methyl phenyl selenone (20 °C, 0.5 h, 75%) but overoxidizes dimethyl selenide[12] (20 °C, 0.5 h) (Table 1). We have also tested the reactivity of these two types of reagents towards a series of dialkyl and alkyl phenyl selenides (Table 2).

Peracids allow the high yield synthesis of di-(primary-alkyl) selenones from the corresponding selenides. Yields of selenones from (primary-alkyl) phenyl selenides are often lower. Generally alkyl phenyl selenides are more difficult to oxidize to selenones than dialkyl selenides are, especially when long alkyl chains are present. In these cases an excess of oxidizing agent often enhances the yield of selenones by increasing the speed of the second oxidation which therefore minimizes the competitive selenoxide elimination reaction. Alkyl phenyl selenones, especially of lower molecular weights, are sensitive to nucleophiles and bases (KOH, $Na_2S_2O_3$, SiO_2 on t.l.c. plates) and therefore the purification of these selenones from the crude mixture is often difficult. Perbenzoic acid and pertrifluoroacetic acid do not allow the synthesis of selenones from (secondary-alkyl) methyl and (secondary-alkyl) phenyl selenides owing to side reactions which include the selenoxide elimination.

The potassium permanganate method offers the advantage of easy recovery of the selenone from the medium since all the by-products are inorganic. This method proved efficient for the synthesis of several dialkyl selenones including (secondary-alkyl) methyl selenones. Unfortunately the first members of the series (dimethyl selenone, ethyl methyl selenone, isopropyl methyl selenone) are not available under these conditions. Moreover, it suffers from severe limitations in the phenylseleno series where the reverse situation is observed. Only the first members of the series, namely methyl phenyl selenide and ethyl phenyl selenide among the ones we have reacted, have been cleanly oxidized to selenones.

These results illustrate the behaviour of various selenides towards different oxidants. Although no general method is available a large number of selenones can be prepared by the proper choice of method. It is unclear if the difficulties encountered are due to the low aptitude of some selenoxides to be oxidized to selenones or to their high reactivity. All the selenones reported exhibit a ^{77}Se n.m.r. signal between +980 and +1040 p.p.m. (dimethyl selenide being used as external reference). Such ^{77}Se chemical shift values are greater by far than that of the corresponding selenoxides and thus consistent with the proposed structures. Moreover an *X*-ray structure determination,† performed on methyl phenyl selenone, confirms this structure unambiguously. Comparison with the corresponding sulphone[22] is presented in Figure 1.

Received, 24th January 1985; Com. 105

References

1 H. Rheinboldt, in 'Houben-Weyl Methoden der Organischen Chemie,' ed. Eugen Müller, Band IX, 1955, Verlag, Stuttgart.
2 D. L. Klayman and W. H. H. Günther, 'Organic Selenium Compounds: Their Chemistry and Biology,' Wiley-Interscience, New York, 1973, pp. 209—211.
3 H. J. Reich, in 'Oxidation in Organic Chemistry,' vol. 5, part C, 1978, p. 1.
4 B. A. Arbusow, *Chem. Zentralbl.*, 1937, **I**, 4943.
5 E. S. Gould and J. D. McCullough, *J. Am. Chem. Soc.*, 1951, **73**, 3196.
6 W. Dilthey and W. Schommer, *J. Prakt. Chem.*, 1930, **124**, 119.
7 R. Lesser and R. Weiss, *Chem. Ber.*, 1913, **46**, 2651.
8 H. Rheinboldt and E. Giesbrecht, *J. Am. Chem. Soc.*, 1946, **68**, 2671.
9 J. Loevenich, H. Fremdling, and M. Fohr, *Chem. Ber.*, 1929, **62**, 2856.
10 L. M. Yagupol'skii and V. G. Voloshchuk, *Zh. Obshch. Khim.*, 1968, **38**, 2509; (English translation) 1968, 2426.
11 R. Paetzold and G. Bochmann, *Z. Anorg. Allg. Chem.*, 1968, **360**, 293.
12 M. L. Bird and F. Challenger, *J. Chem. Soc.*, 1942, 570.
13 G. Ayrey, D. Barnard, and D. T. Woodbridge, *J. Chem. Soc.*, 1962, 2089; B. Lindgren, *Chem. Scr.*, 1980, **16**, 24.
14 I. Kuwajima, R. Ando, and T. Sugawara, *Tetrahedron Lett.*, 1983, **24**, 4429.
15 M. Shimizu, R. Ando, and I. Kuwajima, *J. Org. Chem.*, 1984, **49**, 1230, and references cited.
16 S. Uemura, S-i. Fukuzawa, and A. Toshimutsu, *J. Chem. Soc., Chem. Commun.*, 1983, 1501.
17 K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patrick, S. P. Singer, and M. W. Young, *Chem. Scr.*, 1975, **8A**, 9.
18 D. L. J. Clive, *Tetrahedron*, 1978, **34**, 1049.
19 H. J. Reich, *Acc. Chem. Res.*, 1979, 22.
20 A. Krief, *Tetrahedron*, 1980, **36**, 2531.
21 M. Cinquini, S. Colonna, and R. Giovini, *Chem. Ind.*, 1969, 1737.
22 L. G. Vorontsova, *Sov. Phys. Crystallogr.*, 1965, **10**, 139.
23 G. M. Sheldrick, 'SHELX 76. Program for crystal structure determination,' 1976, University of Cambridge, U.K.

---

† *Crystal data*: $C_7H_8O_2Se$, M_R = 203, monoclinic, space group $P2_1/c$, a = 8.288(2), b = 9.138(3), c = 10.795(2) Å, β = 111.58(2)°, U = 760 Å^3, Z = 4, D_x = 1.77 g cm^{-3}, *X*-ray data were collected using an Enraf-Nonius CAD-4 diffractometer, and Mo-K_α radiation (λ = 0.71069 Å), with 1067 unique observed reflections [with $I > 2.5\sigma(I)$] having $2\theta < 52°$. The structure was solved by Patterson-Fourier and refined by full-matrix least squares to a current residual R of 0.05 (SHELX 76, Sheldrick, 1976, ref. 23).

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.