A Novel, Simple Method for Transformation of C–Se to C–O Bonds

Sakae Uemura,* Shin-ichi Fukuzawa, and Akio Toshimitsu

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Oxidation of alkyl phenyl selenides with *m*-chloroperbenzoic acid in methanol at room temperature affords the corresponding alkyl methyl ethers almost quantitatively, the reaction being accompanied by phenyl migration and ring-contraction respectively when applied to selenides having a phenyl group vicinal to the phenylselenium moiety and to some methoxyselenation products of cyclic olefins.

It is well known that the oxidation of alkyl phenyl selenides with several oxidizing agents readily results in selenoxide elimination leading to olefins.[1] In sharp contrast we have now found that alkyl phenyl selenides are readily and nearly quantitatively converted into alkyl ethers using *m*-chloroperbenzoic acid (MCPBA) as oxidizing agent under mild conditions. To the best of our knowledge this type of transformation (C–Se → C–O) has not yet been fully developed.[1a,2]

$C_{12}H_{25}X$
(1) X = SePh
(2) X = OMe

$C_{12}H_{25}CH(X)Me$
(3) X = SePh
(4) X = OMe

$PhCH(R)CH_2SePh$
(5) R = Me
(6) R = OMe

$MeOCH(R)CH_2Ph$
(7) R = Me
(8) R = OMe

Oxidation of dodecyl phenyl selenide **(1)** with MCPBA (5 equiv.) in methanol at room temperature (20—25 °C) for 1 h afforded dodecyl methyl ether **(2)** almost quantitatively, dodec-1-ene, anisole, and phenol not being detected.† If 2 equiv. of MCPBA was used, **(2)** was obtained in 80% yield, while dodec-1-ene (39% yield) was the sole product when 1 equiv. of MCPBA was used. A similar reaction occurred with the secondary selenide **(3)**, the ether **(4)** produced (90%) being accompanied by small amounts of tetradec-1- and -2-ene (10%). Methanol was the most appropriate solvent; oxidation of **(1)** in solvents such as ethanol, propan-1-ol, and propan-2-ol was slow and even after 24 h a lower yield of **(2)** was obtained (<45%), accompanied by a small amount of dodec-1-ene (<10%).

When a phenyl group was vicinal to the SePh moiety as in **(5)** and **(6)**, the replacement of SePh by OMe was accom-

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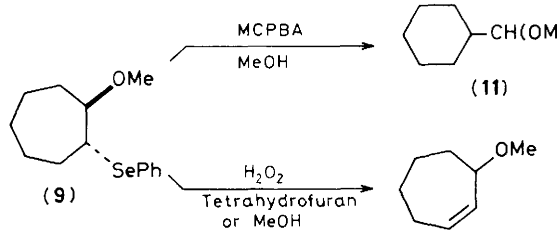
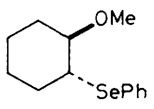
† Other oxidizing agents afforded only dodec-1-ene, as expected, under similar conditions: *e.g.*, treatment of the selenide **(1)** with 5 equiv. of H_2O_2 in MeOH or 5 equiv. of $NaIO_4$ in aqueous MeOH gave dodec-1-ene in 40 and 47% yield, respectively.





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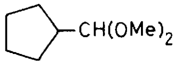

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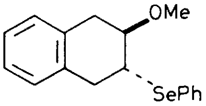

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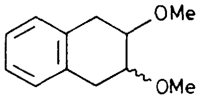
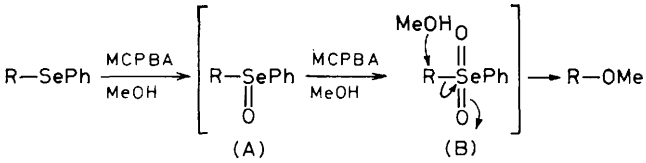


(15)

panied by phenyl migration to give (**7**) and (**8**), respectively, almost quantitatively.

Similarly the products (**9**) and (**10**)[3] of the methoxyselenation of cyclic olefins afforded readily and quantitatively the dimethyl acetals (**11**) and (**12**) of the ring-contracted cyclic aldehydes, whereas the allylic ether (**13**) was obtained quantitatively from (**9**) by use of 5 equiv. of H_2O_2 as oxidizing agent (25 °C for 1 h). It is interesting that in the case of the selenide (**14**)‡ only *ipso*-substitution by the methoxy group occurred to give (**15**) instead of ring-contraction as in the cases of (**9**) and (**10**). This replacement was non-stereospecific [*cis*: *trans* ratio of 4:6 for (**15**)].§



Scheme 1

We suggest that the reaction takes place as in Scheme 1. Since the selenoxide (A) leads only to the olefin, we assume that the reaction involves a further oxidized species, the selenone (B), in which C–Se bond fission may occur, accompanied by concerted attack of methanol, by phenyl migration, or by ring-contraction. A carbocationic intermediate is also possible. MCPBA and/or *m*-chlorobenzoic acid might catalyse the bond cleavage in (B). The oxidation of (A) to (B) by MCPBA seems to be much faster in methanol than in other alcohols and also much faster than oxidation with other oxidizing agents.

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References

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‡ The reaction of 1,4-dihydronaphthalene with PhSeCl in methanol in the presence of Et_3N at 25 °C for 20 h gave (**14**) in 90% yield, stereospecifically, *trans* (^1H n.m.r.).

§ The individual isomers were isolated by preparative t.l.c. (hexane–EtOAc, 4:1, as eluant) and their structures determined by ^1H n.m.r. spectroscopy. Their stereochemistry has only been tentatively assigned as yet.