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# HIGHLY EFFICIENT METHOD FOR OXIDATION OF ALCOHOL WITH *tert* -BUTYL HYDROPEROXIDE CATALYZED BY DIARYL DISELENIDE

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Summary: In the presence of a catalytic amount of diphenyl diselenide (0.1-0.2 eq) *tert*-butyl hydroperoxide oxidized benzylic and primary allylic alcohols in high yields. Saturated alcohols were also cleanly oxidized by the use of bis(2,4,6-trimethylphenyl) diselenide.

To date various procedures have been devised and widely employed for oxidation of primary alcohols into the corresponding aldehydes.[1] However, they sometimes involve use of a large amount of reagents and/or relatively laborious preparations and handlings of the reagents. For example, Collins oxidation, one of the most common procedures, requires a large excess of reagent (6 eq) and solvent,[1b] and highly troublesome work must often be executed for a large scale preparation.

We have recently developed an efficient method for direct transformation of olefins into α-phenylseleno carbonyl compounds.[2] In this reaction, the involvement of an alkylselenenate intermediate, RCH(OSeAr)CH$_2$SeAr, derived from the addition of a [ArSeOSeAr] species 1 to olefins may be responsible for the facile one-step conversion into the carbonyl compounds. During examination of this type of oxidation, we have found a new type of highly efficient system for oxidation of alcohols into the corresponding carbonyl compounds.

In the presence of a catalytic amount of diphenyl diselenide (0.1-0.2 eq) *tert*-butyl hydroperoxide[3] oxidized benzylic and primary allylic alcohols into the corresponding aldehydes in excellent yields (87-100%).

ArSeOSeAr

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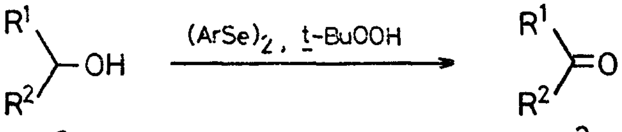


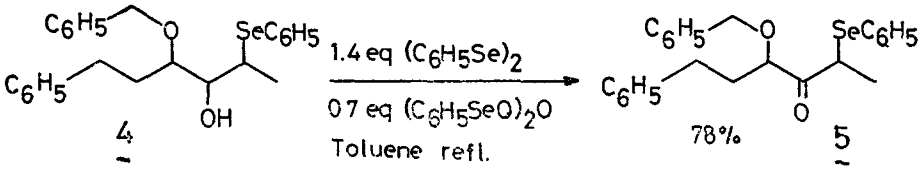
2 3

For the oxidation of saturated alcohols, diphenyl diselenide was not so effective, but the use of bis(2,4,6-trimethylphenyl) diselenide (0.5 eq)[4] proved to be of high efficacy. The effect of diaryl substituents on diselenides has been briefly examined by employing 3-phenyl-1-propanol as the substrate.[5] [Yield of 3-phenylpropanal; 64% with $(C_6H_5Se)_2$, 4% with $(2\text{-}NO_2C_6H_4Se)_2$, 98% with $(2,4,6\text{-}(CH_3)_3C_6H_2Se)_2$ ]. As expected, an electron donating substituent enhanced the reaction rate remarkably, while the reaction did not proceed practically with the diselenide possessing electron attracting nitro group. Because of its easier preparation and the relatively sluggish addition rate of the resulting reactive species to olefinic bonds, bis(2,4,6-trimethylphenyl) diselenide was most suitably employable for the oxidation of a wide range of alcohols.

In general this oxidation proceeded more readily with benzilic and allylic alcohols[6] (87-100%; react period 1-2 hr) than saturated analogues (97-100%; 4-17 hr for ketones, 92-98%; 4-5 hr for aldehydes). This difference shows an interesting tendency as compared with the hitherto reported oxidation reagents.[7]

Olefinic bonds usually survived the reaction conditions of this system.[8,9] Thus, allylic alcohols having another C=C bond (for example, geraniol) were oxidized to the corresponding aldehydes quantitatively. Even in the case of citronellol which is known to undergo a facile oxidative cyclization,[1j] the oxidation could be performed effectively (88% yield) without affecting the double bond using a small amount of secondary amine (0.3 eq).[10,11]

Moreover, benzeneseleninic anhydride and diphenyl diselenide[2b] were shown to oxidized the following β-hydroxyselenide **4** efficiently into the desired α-phenylseleno ketone **5** which could be isolated in only a very poor yield by Collins oxidation.[12]



The operational simplicity of the procedure of the present system both on small and large scale oxidations has been demonstrated by the following typical exmples.

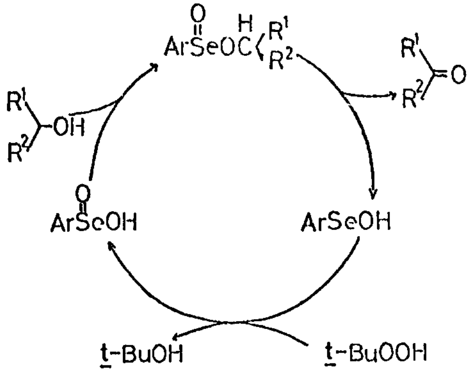
Geranial (small scale preparation)

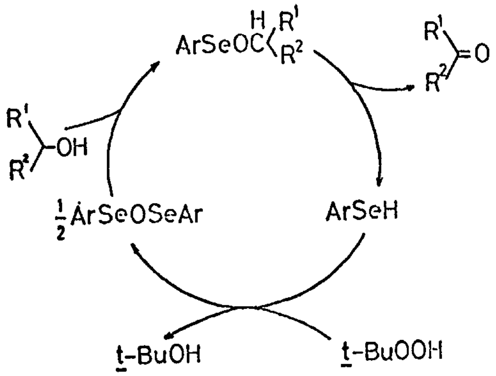
To a benzene (2 ml) solution of bis(2,4,6-trimethylphenyl) diselenide (198 mg, 0.5 mmol) were added successively solutions of 70% *tert*-butyl hydroperoxide (141 mg, 1.1 mmol) in 3 ml of benzene and geraniol (154 mg, 1.0 1.0 mmol) in 5 ml of benzene. After stirring for 1 h under reflux, the solvent was removed by evaporation and the remaining yellow oil was purified on silica gel column chromatography to afford the diselenide (161 mg, 81% recovery) and the title compound (151 mg, 100%). Glpc analysis[13] indicated that geranial (98%) and neral (2%) were formed.

Decanal (large scale preparation)

To a refluxing solution of bis(2,4,6-trimethylphenyl) diselenide (19.8 g, 50 mmol) and 1-decanol (15.8 g, 100 mmol) in 150 ml of benzene was added a benzene (50 ml) solution of 70% *tert*-butyl hydroperoxide (18.2 g, 150 mmol) during 30 min. After stirring for 5 h under refluxing the reaction mixture was washed with satd aq $Na_2CO_3$ and brine. Separation and removal of the solvent gave an orange-colored oil, which was distilled to afford the title compound (14.4 g, 92%).[14] The spectroscopic and glpc analyses were identical with the authentic sample.

Although the reaction course is not very clear at present time, there appear to be two possible explanations. The following equations may illustrate possible mechanisms.[15,16]





Further, a simple operational procedure, especially for a large scale preparation, repeatable utility of the diselenide recovered well,[14] and a tolerance for functional groups appear to make this new method a useful addition to the previous methodologies.

We are currently studying this type of reactions in more details to establish an entirely catalytic oxidation method of alcohols.

## References and Notes

(1) (a) W.W.Epstein and F.W.Sweat, Chem.Rev., **67**, 247 (1967), and references cited therein; (b) T.C.Collins, W.W.Hess, and F.J.Fran, Tetrahedron Lett., 3363 (1968); (c) E.J.Corey and C.V.Kim, J.Am.Chem.Soc., **94**, 7586 (1972); (d) E.J.Corey and J.W.Suggs, Tetrahedron Lett., 2647 (1975); (e) K.B. Sharpless and K.Akashi, J.Am.Chem.Soc., **97**, 5927 (1975); (f) K.Omura, A.K.Sharma, and D.Swern, J.Org.Chem., **41**, 957 (1976), and references cited therein; (g) K.B.Sharpless, K.Akashi, and K.Oshima, Tetrahedron Lett., 2503 (1976); (h) K.Saigo, A.Morikawa, and T.Mukaiyama, Bull.Chem.Soc.Jpn.,

**49**, 1656 (1976); (i) G.Cainelli, G.Cardillo, M.Orena, and S.Sandri, *J.Am.Chem.Soc.*, **98**, 6737 (1976); (j) E.J.Corey and D.L.Boger, *Tetrahedron Lett.*, 2461 (1978); (k) E.J.Corey and G.Schmidt, *ibid.*, 399 (1979).

(2) (a) I.Kuwajima and M.Shimizu, *Tetrahedron Lett.*, 1277 (1978); (b) M.Shimizu, R.Takeda, and I.Kuwajima, *ibid.*, 419 (1979).

(3) K. B. Sharpless and his collaborators have also observed diaryl diselenide catalyzed oxidation of alcohols with *tert*-BuOOH or $ArSO_2NClNa$; private communication from Prof. K. B. Sharpless.

(4) In the case of saturated alcohols, the oxidation did not proceed with a reasonable rate in the presence of less than 0.3 eq of diaryl diselenide. This may in part arise from a simultaneous decomposition of *t*-BuOOH by diselenide; D.T.Woodbridge, *J.Chem.Soc.*, (B), 50 (1966).

(5) Relative rates of oxidation of some diselenides were reported; G.Ayrey, D.Barnard, and D.T.Woodbridge, *J.Chem.Soc.*, 2089 (1962).

(6) Despite some susceptibility of allyl selenenate to isomerization into allyl selenoxide, no rearranged product was obtained; H.J.Reich, I.L.Reich, and S.Wollowitz, *J.Am.Chem.Soc.*, **100**, 5981 (1978).

(7) A similar tendency was observed in the ruthenium catalyzed oxidation; ref. 1g.

(8) According to the previously reported procedure (ref 2b), 1-decene was oxidized to 1-phenylseleno-2-decanone (48%) and 2-phenylseleno-1-decanal (22%).

(9) $[C_6H_5SeOH]$ species was reported to add readily to olefins; (a) T.Hori and K.B.Sharpless, *J.Org.Chem.*, **43**, 1689 (1978); (b) H.J.Reich, S.Wollowitz, J.F.Trend, F.Chow, and D.F.Wendelborn, *ibid.*, **43**, 1697 (1978); (c) D. Labar, A.Krief, and L.Hevesi, *Tetrahedron Lett.*, 3967 (1978).

(10) In the absence of secondary amines cyclization (see, ref 1d) and oxidation of olefin accompanied.

(11) The use of secondary amines sometimes prevents side reactions in the selenoxide elimination; H.J.Reich, M.J.Regna, and I.L.Reich, *J.Am.Chem. Soc.*, **97**, 5934 (1975).

(12) Only 2% of the desired product **5** was obtained by Collins oxidation.

(13) The column [3 mm x 1 m, PEG on Diasolid] was used.

(14) The pure diselenide was recovered about 70% from the distillation residue. It could be used repeatedly without any appreciable decrease of the yield.

(15) K.B.Sharpless and R.F.Lauer, *J.Am.Chem.Soc.*, **84**, 7154 (1972).

(16) Recently, benzeneseleninic anhydride has also been shown to be an efficient reagent for oxidation of alcohols; D.H.R.Barton, A.G.Brewster, R.A.H.F.Hui, D.J.Lester, and S.V.Ley, *J.Chem.Soc. Chem.Commun.*, 952 (1978)

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