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SELECTIVE OXIDATION OF HYDROXY GROUPS OF PHENYLTHIO AND PHENYLSELENO ALCOHOLS

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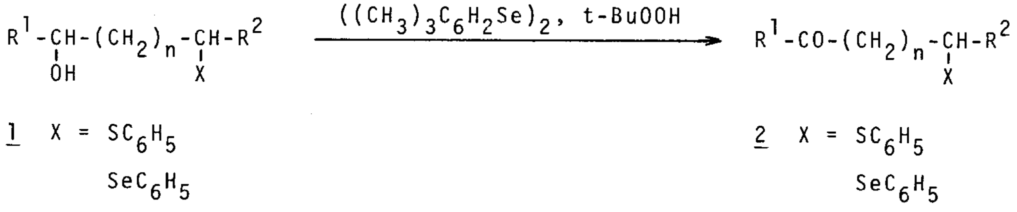
Summary: Various kinds of alcohols bearing phenylthio or phenylseleno moiety were converted into the corresponding carbonyl compounds in good to excellent yields by treating with dimesityl diselenide and tert-butyl hydroperoxide.

Although α-phenylseleno carbonyl compounds,[1] or β-phenylthio and β-phenylseleno enals[2] have recently been employed as versatile reagents in synthetic organic chemistry, their general preparations from the corresponding alcohols through oxidation have been highly difficult, accompanying the simultaneous oxidation at sulfur or selenium moieties.[3] For the oxidation of β-hydroxy selenides,[4] only reported examples involve the use of Corey-Kim[3a] method or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),[3a] aluminum surface oxidation,[3b] and organobismuth oxide.[3c]

We have recently reported the oxidation of alcohols with diaryl diselenide--tert-butyl hydroperoxide system, and briefly described some efficacy of this method for the oxidation of a phenylseleno alcohol.[5] Further examination has revealed that this method is applicable for oxidation of a wide range of alcohols having phenylthio or phenylseleno groups with high selectivity using dimesityl diselenide (0.5∿0.6 equiv) and tert-butyl hydroperoxide (1.3∿1.5 equiv).



$$R^1\text{-}\underset{\text{OH}}{\text{CH}}\text{-}(CH_2)_n\text{-}\underset{X}{\text{CH}}\text{-}R^2 \xrightarrow{((CH_3)_3C_6H_2Se)_2,\ t\text{-BuOOH}} R^1\text{-CO-}(CH_2)_n\text{-}\underset{X}{\text{CH}}\text{-}R^2$$

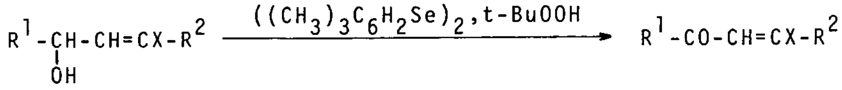
1 X = SC_6H_5
SeC_6H_5

2 X = SC_6H_5
SeC_6H_5

The preparation of 2-phenylselenocyclododecanone represents a typical procedure: A solution of dimesityl diselenide (119 mg, 0.3 mmol) and 70% *tert*-butyl hydroperoxide (96 mg, 0.75 mmol) in benzene (3 ml) was heated to refluxing for 10 min. Then a solution of 2-phenylselenocyclododecanol (170 mg, 0.5 mmol) in benzene (3 ml) was added to the mixture and it was stirred under refluxing for 40 min. The crude reaction mixture was washed with satd. aqueous NaCl and the aqueous layer was extracted with ether. Drying and concentration of the combined extracts gave an orange-colored oil, which was purified by preparative TLC to afford 2-phenylselenocyclododecanone (169 mg, 100%) and recovered dimesityl diselenide (96 mg, 79%).

As shown in Table 1, various kinds of hydroxy groups can be converted into the corresponding carbonyl groups in good to excellent yields, while sulfur or selenium moieties almost survive the reaction conditions. A comment must be added on the possible side reaction; in the case with the formation of a phenylselenomethyl ketone, accompanying selenenylation reaction with reactive species (presumably ArSeOSeAr) was observed, and an appreciable amount of the corresponding α,α-diarylselenomethyl ketone, $R\text{-}CO\text{-}CH(SeC_6H_5)\text{-}SeC_6H_2(CH_3)_3$, was formed as the by-product.

Successful application of the present system to the selective oxidation of 3-phenylthio- and 3-phenylseleno-2-propen-1-ol derivatives 3 should be more remarkable. In connection with our continuing studies on the vinyl selenoxides[6] and vinyl selenones,[2] transformation of such kind of alcohol 3 (R^1 = H, X = SeC_6H_5) to the corresponding aldehyde 4 (R^1 = H, X = SeC_6H_5) was required. To our best knowledge, there is no simple and reliable procedure available for such transformation, although the use of a large excess of active manganese dioxide appears to meet with moderate success in the case of 3 (R^1 = R^2 = H, X = SC_6H_5).[7] Examination of oxidation with pyridinium chlorochromate (PCC) did not give any satisfactory results, but the present dimesityl diselenide--*tert*-butyl hydroperoxide system has been proved to be very effective, giving α,β-unsaturated carbonyl compounds 4 in high yields as shown in Table 2.



$$R^1\text{-}\underset{\displaystyle OH}{CH}\text{-}CH{=}CX\text{-}R^2 \xrightarrow{((CH_3)_3C_6H_2Se)_2,\,t\text{-}BuOOH} R^1\text{-}CO\text{-}CH{=}CX\text{-}R^2$$

3 X = SC_6H_5
SeC_6H_5

4 X = SC_6H_5
SeC_6H_5

Table 1. Oxidation of 1 to 2.

Alcohol 1				React. Period	
R^1	R^2	n	X	(min)	Yield[a] of 2,%
$-(CH_2)_4-$		0	SeC_6H_5	180	79
$-(CH_2)_6-$		0	SeC_6H_5	15	91
$-(CH_2)_{10}-$		0	SeC_6H_5	40	100
C_4H_9	C_4H_9	0	SeC_6H_5	40	90
H	H	4	SeC_6H_5	120	86
H	C_4H_9	0	SeC_6H_5	60	58
$C_{10}H_{21}$	H	0	SeC_6H_5	90	66
$-(CH_2)_{10}-$		0	SC_6H_5	90	72

[a] Isolated yield.

Table 2. Oxidation of 3 to 4.

Alcohol 3			React. Period	
R^1	R^2	X	(min)	Yield[a] of 4,%
H	H	SC_6H_5	45	100
H	H	SeC_6H_5	45	90
H	CH_3	SC_6H_5	45	55[b]
H	CH_3	SeC_6H_5	90	64[b]
H	C_6H_{13}	SC_6H_5	10	78[c]
$-CH_2C(CH_3)_2CH_2-$		SeC_6H_5	15	88

[a] Isolated yield. [b] Crude yield. [c] The reaction was performed in isopropyl acetate in the presence of KH_2PO_4(2.4 eq).

In conclusion, the present method offers a convenient and reliable procedure for the transformation of alcohols to carbonyl compounds in the presence of phenylthio or phenylseleno groups, and is extremely useful for large scale preparation because of a nearly stoichiometric amount of the oxidizing reagent required. Especially for the preparation of β-phenylthio and β-phenylseleno enals (or enones), this system has turned out to be the best method of transformation from the corresponding alcohols.

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