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OXYGEN INDUCED REDUCTION: REACTION OF BENZENESELENOL WITH AROMATIC ALDEHYDES IN THE PRESENCE OF OXYGEN

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ABSTRACT

Reduction of aromatic aldehydes by benzeneselenol is found to be promoted by molecular oxygen to give corresponding alcohols in good yields. No reduction took place without oxygen.

A free radical process involving S_H2 reaction at the selenium atom is proposed where the phenylseleno radical attacks the selenium atom of selenohemiacetal, the adduct of benzeneselenol to aldehyde, to give the ketyl radical which then abstracts hydrogen from benzeneselenol. The intermediacy of selenohemiacetal is supported by a quantitative reduction of α-methoxybenzyl phenyl selenide, which is used as a model compound of the intermediate.

INTRODUCTION

During the course of our study on the reactivity of benzeneselenol (**I**),[1] we found that benzeneselenol shows a unique reducing ability toward some olefinic compounds when oxygen is present. For example, the reaction of α,β-unsaturated carbonyl compounds[2] with benzeneselenol in the presence of oxygen results in the selective reduction of the carbon–carbon double bond to give corresponding saturated carbonyl compounds. It has been suggested the reduction involves a radical chain mechanism initiated by oxygen. We now wish to report that the present benzeneselenol–oxygen reduction system is also useful for reduction of aromatic aldehydes to the corresponding alcohols.

$$\underset{\textbf{II}}{XC_6H_4CHO} \xrightarrow{PhSeH\ /\ O_2} \underset{\textbf{III}}{XC_6H_4CH_2OH}$$

A typical example of the reduction in the presence of oxygen is given below. In a sealed apparatus filled with nitrogen, were placed benzaldehyde (**IIa**, 1 mmol, 106 mg), dry degassed benzene (2·5 ml), and benzeneselenol (3 mmol, 471 mg). At this stage, reduction did not take place (10 °C, 20 h). However, when oxygen (20 mol%) was admitted into the apparatus, the

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Table 1. Reduction of aromatic aldehydes with benzeneselenol

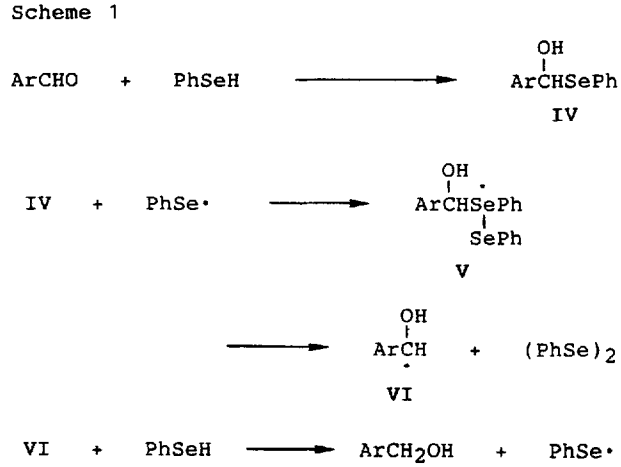
entry		substrate X	additive	mol%	yield, % III
1[a]	**IIa**	H	none		trace
2[a]			O_2	4	trace
3[a]				10	43
4[a]				20	63
5[b]	**IIb**	*p*-Cl	air		62
6[b]	**IIc**	*p*-CF_3			38
7[b]	**IId**	*p*-CH_3O			86
8[b]	**IIe**	*p*-CH_3			59
9[b]	**IIf**	*m*-CH_3			89
10[b]	**IIg**	*o*-CH_3			94
11[c]	**IIa**	H	AIBN	10	18
12[c]				50	55
13[c]				100	63

[a] 10 °C, 20 h in benzene.
[b] 10 °C, 20 h in Et_2O under air atmosphere.
[c] 110 °C, 1 h in toluene.

reduction started and benzyl alcohol (**IIIa**) was obtained as a reduction product in 63% yield. The by-product was diphenyl diselenide. Results obtained from several aromatic aldehydes are summarized in Table 1. The yield of the alcohol increases with increase in the amount of oxygen (entries 2–4, Table 1).

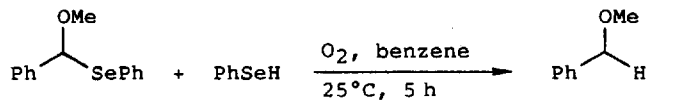
That the reaction is initiated by a free radical process is apparent since similar reduction of benzaldehyde with benzeneselenol has proceeded by use of 2,2′-azobisisobutyronitrile (AIBN) in refluxing toluene under nitrogen (entries 11–13, Table 1). A proposed mechanism for the present reduction is given in Scheme 1. Initially, addition of benzeneselenol to aldehyde takes place to give an adduct **IV** (It is known that thiols readily react with aldehydes to form thiohemiacetals).[3] The equilibrium between **IVa** and the starting materials has been confirmed in the absence of oxygen by ^{1}H-NMR. The adduct **IVa** showed singlet peaks at δ

Scheme 1



6·58 and δ 4·26 which can be assigned to benzylic and hydroxyl protons, respectively. The adduct **IV** then reacts with phenylseleno radical, which is generated by the reaction of benzeneselenol with oxygen,[4] in S_H2 manner to give phenylhydroxymethyl radical (**VI**) and diphenyl diselenide via an intermediate radical **V**. The radical **VI** readily abstracts a hydrogen atom from benzeneselenol to afford benzyl alcohol and phenylseleno radical. Noteworthy is that the radical **VI** seems to have reacted exclusively with benzeneselenol even in the presence of oxygen which is known as a radical scavenger. The extraordinarily high hydrogen transfer ability[5] of benzeneselenol must be a key to the success of the present oxygen induced reduction to take place.

As a model compound of **IV**, a methoxy derivative **VII** was prepared and subjected to reaction with benzeneselenol and oxygen. Clean reduction to benzyl methyl ether was observed.



VII quantitative

Neither aliphatic aldehydes (e.g. phenylacetaldehyde, nonanal) nor ketones (e.g. acetophenone, cyclohexanone) were reduced under the present reaction conditions. This may be due to the lack of sufficient stability of corresponding ketyl radical intermediate which affects the S_H2 process in the former case and to steric repulsion in the addition process in the latter case. This quite high sensitivity of the present reduction on the structure of the substrate led us to attempt selective reduction of aromatic aldehydes in the presence of other carbonyl compounds. As a typical example, we have succeeded in selective reduction of benzaldehyde to benzyl alcohol in the presence of acetophenone which remained unchanged under similar conditions. However, when the reaction was run without a solvent, acetophenone was reduced to the corresponding alcohol to some extent, probably because the disadvantage of addition due to steric hindrance has been overcome by higher concentration of materials.

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REFERENCES

1. Some reactions in which benzeneselenol acts as a reducing agent are known: (a) W. H. H. Günther, *J. Org. Chem.* **31**, 1202 (1966). (b) K. Fujimori, H. Yoshimoto, and S. Oae, *Tetrahedron Lett*, 4397 (1979). (c) K. Fujimori, H. Yoshimoto, and S. Oae, *Tetrahedron Lett.* **21**, 3385 (1980). (d) F. G. James, M. J. Perkins, O. Porta, and B. V. Smith, *J. Chem. Soc., Chem. Commun.* 131 (1977). (e) M. J. Perkins, B. V. Smith, B. Terem, and E. S. Turner, *J. Chem. Res. (S)* 341 (1979). (f) M. J. Perkins, B. V. Smith, and E. S. Turner, *J. Chem. Soc., Chem. Commun.* 977 (1980).
2. T. Masawaki, *et al. J. Phys. Org. Chem.*, **1**, 115–117 (1988).
3. See, for example, T. J. Burkey and R. C. Fahey, *J. Am. Chem. Soc.* **105**, 868 (1983) and references cited therein.
4. *Organic Selenium Compounds: Their Chemistry and Biology*, D. L. Klayman, and W. H. H. Günther, Wiley, New York (1973). A. Fava, G. Reichenbach, and U. Peron, *J. Am. Chem. Soc.* **89**, 6696 (1967).
5. N. Kambe, *et al. Chem. Lett.* 1907 (1987).