JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 1, 115-117 (1988)

SHORT COMMUNICATIONS

A NOVEL OXYGEN INDUCED REDUCTION OF α,β-UNSATURATED CARBONYL COMPOUNDS BY BENZENESELENOL

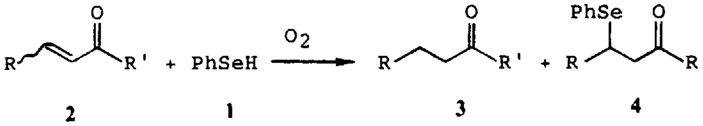
TERUYUKI MASAWAKI, YUZO UCHIDA, AKIYA OGAWA,
NOBUAKI KAMBE, NORITAKA MIYOSHI, AND NOBORU SONODA*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

ABSTRACT

A novel oxygen induced reduction of α,β-unsaturated carbonyl compounds is discovered. The reduction of the carbon–carbon double bond of α,β-unsaturated carbonyl compounds by benzeneselenol was caused by an introduction of molecular oxygen into the reaction system. This reduction is likely to proceed via a radical chain pathway involving an S_H2 type reaction between a phenylseleno radical and a 1,2-adduct of benzeneselenol to the carbonyl group of the α,β-unsaturated carbonyl compound to give an allylic radical which absracts a hydrogen atom from benzeneselenol to form the reduction product.

INTRODUCTION

It is generally agreed that molecular oxygen should be excluded from the reaction media when reduction is to be performed. To the best of our knowledge, there exist few examples in which oxygen induces or accelerates reduction. (In the diimide reduction, oxygen has been used for the generation of diimide, NH=NH, from hydrazine.)[1] During the course of our study on the reactivity of benzeneselenol (**1**), we found that the reduction of the carbon–carbon double bond of α,β-unsaturated carbonyl compounds with benzeneselenol (some reactions in which benzeneselenol acts as a reducing agent are known)[2] was caused by an action of molecular oxygen to afford corresponding saturated carbonyl compounds. We wish to report here this very rare case in which oxygen promotes the reduction.



A typical example is as follows. Benzeneselenol (13 mmol) was added to a dry degassed 1,2,3,4-tetrahydronaphthalene (25 ml) solution of 2–butenal (**2a**, 13 mmol) and the mixture was stirred at 40 °C for 5 h in a sealed apparatus. Without oxygen, Michael type addition occurred predominantly to give 3-phenylselenobutanal (**4a**) in 42% yield.[3] Interestingly,

---

*Author for correspondence.

0894–3230/88/020115–03$05.00

Received 2 November 1987

however, when a small amount of oxygen was introduced into the apparatus, the reduction of the carbon–carbon double bond took place competitively to yield butanal (**3a**, 27% in the case of 6 mol% of oxygen and 39% for 27 mol% of oxygen) as well as **4a**. Noteworthy is that the yield of the reduction product increases with increase in the amount of oxygen.

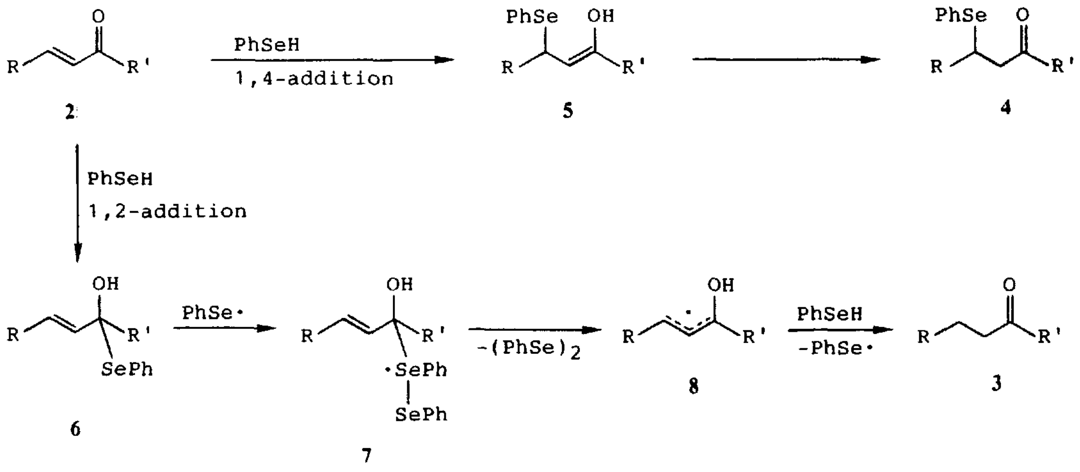
Similar oxygen induced reduction reactions of several α,β-unsaturated aldehydes and ketones by benzeneselenol have been conveniently performed in air. Representative results are summarized in Table 1.

Table 1. Reaction of α,β-unsaturated carbonyl compounds with benzeneselenol in the presence of oxygen

	substrate		yield, %	
	R	R′	**3**	**4**
2a	CH_3	H	51	9
2b	H	H	35	38
2c	Ph	H	86	14
2d	H	CH_3	11	63
2e	CH_3	CH_3	16	43
2f	Ph	CN	49	51

The intermediacy of the Michael type adduct (**4**) in the reduction pathway is clearly ruled out by the fact that reduction products (**3**) were not obtained from the reaction of **4** with benzeneselenol under similar conditions. Since it is likely that the phenylseleno radical is formed in the reaction system by the reaction of benzeneselenol with oxygen (it is known that benzenethiol reacts with oxygen to give thiyl radical in first order on each component),[4] the present reduction is suggested to proceed via a free radical pathway. A plausible reaction path is shown in the Scheme. At the initial stage, 1,4- and 1,2-addition of benzeneselenol to α,β-unsaturated carbonyl compounds afford **5** and **6**, respectively, and 1,4-adduct (**5**) isomerizes immediately to a Michael type adduct (**4**). In the presence of oxygen, only the 1,2-adduct (**6**) undergoes further S_H2 type reaction by the attack of phenylseleno radical onto the selenium atom of **6**. The elimination of diphenyl diselenide from **7** gives a relatively stable allylic radical intermediate (**8**), which then abstracts hydrogen from benzeneselenol to yield saturated carbonyl compounds. Phenylseleno radical regenerated at the last stage may cause the chain reaction. This mechanism is supported by the following facts. i) The reaction of saturated carbonyl compounds with benzeneselenol undergoes 1,2-addition smoothly in the similar reaction system, for example, 1-phenylseleno-3-phenylpropan-1-ol can be isolated by the reaction of 3-phenylpropanal with benzeneselenol. ii) The phenylseleno-group of cinnamyl phenyl selenide ($PhCH{=}CHCH_2SePh$), a model compound of **6**, is replaced with hydrogen under the similar conditions.

The reduction of enones proceeded in lower yields than that of enals, probably because the initial formation of selenohemiacetal (**6**) is suppressed due to the bulkiness of the alkyl group on the enone. It should be recalled that carbon radicals generally undergo dimerization or react with molecular oxygen when oxygen is present. However in the present reduction, such reactions are not observed and carbon radicals abstract hydrogen from benzeneselenol exclusively. This may be due to a weak Se—H bond energy of benzeneselenol. We have



Scheme

already demonstrated that hydrogen selenide transfers hydrogen quite rapidly toward a variety of carbon radicals and the rate constant of hydrogen transfer to the secondary carbon radical has been estimated to be about $1{\cdot}6 \times 10^8$ $\mathrm{M}^{-1}\mathrm{s}^{-1}$.[5] It is likely that the H—Se bond energy of PhSeH should be smaller than that of H_2Se (73kcal/mol),[6] since H—S bond energy of PhSH (82kcal/mol)[7] is smaller than that of H_2S (91kcal/mol)[8] by about 9kcal/mol. This extraordinarily high hydrogen transfer ability of benzeneselenol must be a key to the success of the present oxygen induced reduction to take place.

ACKNOWLEDGEMENT

This work was supported in part by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1. E. J. Corey, W. L. Mock, and D. J. Pasto, *Tetrahedron Lett.* **21**, 347 (1961).
2. (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).
3. N. Miyoshi, *et al.*, *Synthesis* 300 (1979). M. Miyashita and A. Yoshikoshi, *Synthesis* 644 (1980), and references cited therein.
4. A. Fava, G. Reichenbach, and U. Peron, *J. Am. Chem. Soc.* **89**, 6696 (1967).
5. N. Kambe, *et al.*, *Chem. Lett.* 1907 (1987).
6. K. W. Bagnall, *The Chemistry of Sulphur, Selenium, Tellurium and Polonium*, Pergamon Press, New York (1973), p. 954.
7. S. W. Benson, *Chem. Rev.* **78**, 23 (1978).
8. R. T. Sanderson, *Chemical Bonds and Bond Energy*, 2nd Ed., Ed. E. M. Loebl, Academic Press, New York (1976), p. 167.