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Diphenyl Diselenide-Promoted Radical Addition of Benzeneselenol to Acetylenes

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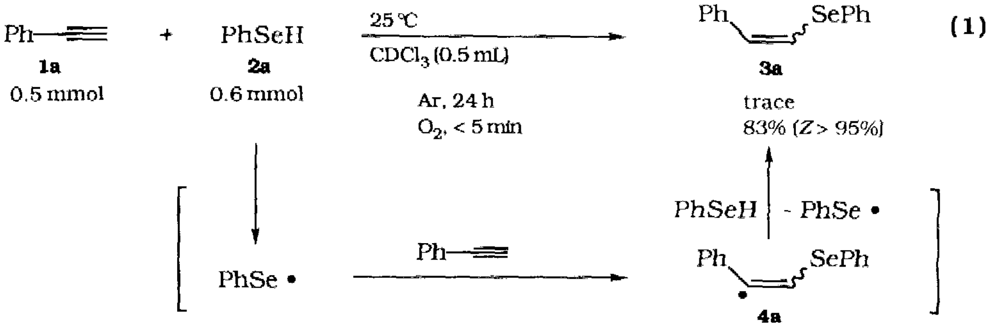
Abstract: *Diphenyl diselenide promotes the radical addition of benzeneselenol to inactivated acetylenes upon irradiation through Pyrex with a tungsten lamp. The addition may proceed by a radical chain mechanism that involves phenylseleno radical (PhSe•) as the key species, generated by the photolysis of* $(PhSe)_2$.

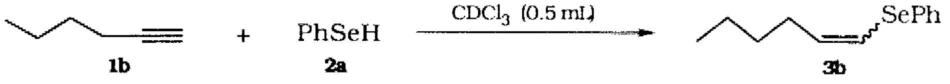
The addition of organic selenols to acetylenes is widely accepted as one of the most straightforward access to vinyl selenides.1) Nevertheless, the inefficiency of the addition to inactivated acetylenes and the mechanistic ambiguity still remain significant problems. For example, the addition of benzeneselenol to 1-hexyne was reported to take longer time (240 h) at room temperature, providing 1-(phenylseleno)-1-hexene in 45 % yield (Z-isomer: >95).2,3) As to the mechanism, one may even be tempted to think that the addition proceeds *via* a radical chain mechanism, but there exists only very limited evidence to support such a possibility.4)

Recently, we have developed the oxygen-induced radical reactions of benzeneselenol, in which phenylseleno radical (PhSe•) formed by hydrogen-abstraction from benzeneselenol by oxygen, acts as the key species.5) Similarly, the addition of organic selenols to acetylenes may be explained by the radical reaction induced by trace amounts of oxygen contained in the reaction system. This hypothesis prompted us to examine the effect of oxygen on the addition of benzeneselenol **2a** to phenylacetylene **1a**: In a sealed tube filled with



argon, were placed phenylacetylene(0.5 mmol), dry degassed $CDCl_3$ (0.5 mL), and benzeneselenol (0.6 mmol). The mixture was kept at 25 °C for 24 h in the dark. The measurement of ^1H NMR spectrum at this stage indicated that the addition reaction hardly proceeded. However, when air (O_2 <10 mol%) was introduced into the apparatus, the addition started and 2-(phenylseleno)-styrene (**3a**) was obtained in 83 % yield within 5 min (Eq. 1). These facts unambiguously indicate our postulate that the addition proceeds by the radical chain mechanism involving the formation of phenylseleno radical by hydrogen-abstraction with oxygen contained.

In contrast to phenylacetylene, the radical-addition to inactivated acetylenes like 1-hexyne proceeded very slowly even in the presence of oxygen. This may be mainly due to the shorter chain-length. In other words, the instability of inactivated vinyl radicals[6)] contributes the inefficiency of the desired addition, and consequently the coupling reaction of seleno radicals to corresponding diselenides takes place preferentially. As an approach to solving this problem, the addition of benzeneselenol to acetylenes was attempted *in the presence of a catalytic amount of diphenyl diselenide under photo-irradiation conditions,* since the photolysis of diselenides can generate seleno radicals continuously.[7)] The addition of benzeneselenol to 1-hexyne (**1b**) proceeded smoothly in $CDCl_3$ in the presence of 10 mol% of diphenyl diselenide upon irradiation through Pyrex with a tungsten



1b 0.5 mmol **2a** 0.6 mmol **3b** (2)

run	conditions	yield
1	Ar/25°C/24 h	no reaction
2	O_2/25°C/24 h	trace
3	10 mol% $(PhSe)_2$/hv (tungsten lamp, 500W, Pyrex)/40°C/3.5 h	78% [*E*/*Z* = 18/82]

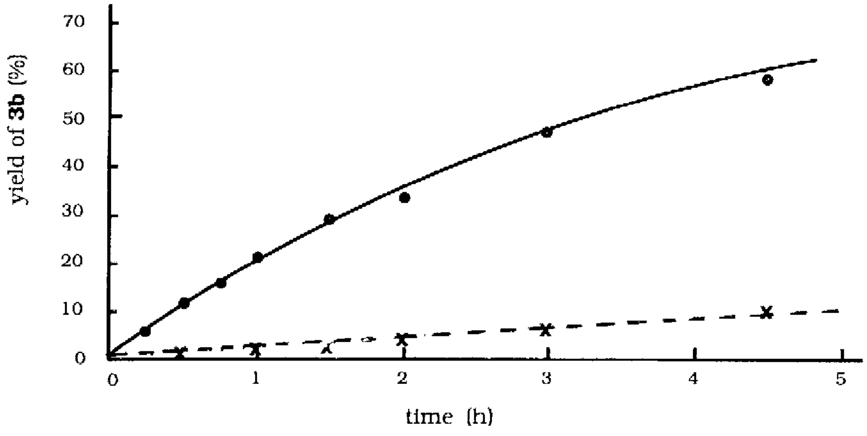
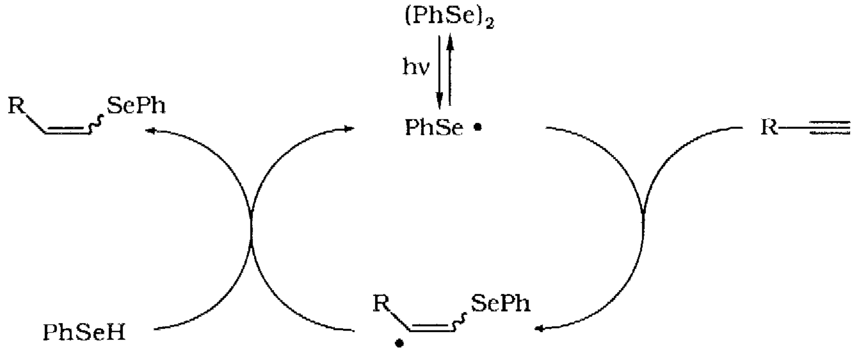


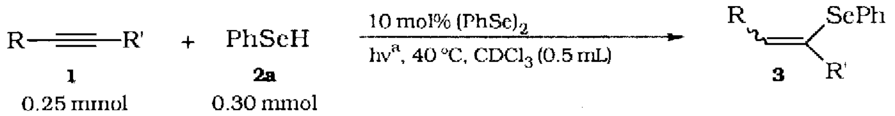
Fig. 1 Yields of **3b** versus reaction time in the presence and absence of diselenide. The reaction was performed by irradiation through Pyrex with a tungsten lamp (200W).[9)] The solid line: in the presence of 10 mol% of diselenide catalyst. The dotted line: in the absence of diselenide.

lamp (500W) to give 1-(phenylseleno)-1-hexene (**3b**) in good yield (Eq. 2). In this case, the 1,2-bis(phenylseleno)-1-hexene was not formed.[8] The yields of **3b** versus reaction time in both the presence and absence of diphenyl diselenide are given in Fig. 1,[9] which clearly indicates the excellent acceleration ability of the diselenide. The formation of a small amount of **3b** in the reaction in the absence of diselenide is explained by the photolysis of benzeneselenol itself leading to phenylseleno radical.[10,11] Needless to say, the addition did not proceed in the dark under argon even in the presence of $(PhSe)_2$. A catalytic reaction path is shown in Scheme 1.



Scheme 1. A Catalytic Reaction Path

As with **1b**, the diselenide-promoted addition of benzeneselenol to some other inactivated acetylenes was performed, and *anti*-Markovnikov adducts were successfully obtained as shown in Eq. 3.[12]



(3)

run	R	R'	time, h	yield, %[b]	E/Z
1	$HOCH_2$	H	5	62 (84)	64/36
2	H_2NCH_2	H	9	(77)	19/81
3	Me_3Si	H	30	44	93/7
4	Ph	*n*-Pr	9	62 (93)	0/100
5	*n*-Pr	*n* Pr	110	(52)[c]	25/75

[a] hv: tungsten lamp (500W, Pyrex). [b] Isolated (NMR) yield. [c] 4-(Phenylseleno)-3-octene (24%, E/Z = 38/62) was formed as byproduct.

In conclusion, this paper provided an evidence that the addition of benzeneselenol to acetylenes under neutral condition proceeded *via* a radical chain mechanism, and moreover, the presence of a catalytic amount of diselenide upon irradiation brought about the efficient addition of benzeneselenol to inactivated acetylenes.

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2) J. V. Comasseto, J. T. B. Ferreira, and N. Petragnani, *J. Organomet. Chem.*, **216**, 287 (1981).

3) Reaction time can be reduced to 24 h at higher temperature (120 °C, yield<70 %), but the seteroselectivity was lost (*E*/*Z* = 50/50), see reference 2.

4) The addition of benzeneselenol to phenylpropiolate ($PhC{\equiv}CCO_2Et$) under neutral condition was reported to provide α-(phenylseleno)cinnamate, whereas the same reaction under basic condition led to β-(phenylseleno)cinnamate. A radical mechanistic pathway was suggested to account for the regiochemistry of the addition under neutral condition, see: D. H. Wadsworth and M. R. Detty, *J. Org. Chem.*, **45**, 4611 (1980).

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8) Radical addition of diselenide to unactivated acetylenes proceeded very slowly in solvent: A. Ogawa, H. Yokoyama, K. Yokoyama, T. Masawaki, N. Kambe, and N. Sonoda, *J. Org. Chem.*, **56**, 5721 (1991).

9) The reaction of 1-hexyne with benzeneselenol (1.2 equiv.) in the presence or absence of diphenyl diselenide (10 mol%) was conducted by irradiation at 40 °C with a tungsten lamp (200W) positioned approximately 20 cm from the Pyrex glass tube. The yield of **3b** in Fig. 1 is lower than that in Eq. 2. This is due to the lightness of tungsten lamp used (200W or 500W). The *E*/*Z* ratio of **3b** for 4.5 h-irradiation is 28/72.

10) A. Mangini, A. Trombetti, and C. Zauli, *J. Chem. Soc.*, (B), **1967**, 153.

11) Benzeneselenol is known to form phenylseleno radical by irradiation with visible light, see: M. J. Perkins, B. V. Smith, and E. S. Turner, *J. Chem. Soc., Chem. Commun.*, **1980**, 977.

12) Typical procedure for diselenide-promoted addition of benzeneselenol to acetylenes is as follows: In a glass tube (Pyrex, ϕ = 5 mm) filled with argon, were placed diphenyl diselenide (8 mg, 0.025 mmol), 1-phenyl-1-pentyne (36 mg, 0.25 mmol), benzeneselenol (47 mg, 0.30 mmol), and dry degassed $CDCl_3$ (0.5 mL), and the tube was sealed. The mixture was irradiated with a tungsten lamp (500W) approximately 8 cm from the tube at 40 °C for 9 h. The solvent was removed in vacuo, and the residual mixture was treated with preparative TLC (silica gel, hexane/Et_2O = 10/1) to provide 46 mg (62 %) of (Z)-1-phenyl-2-(phenylseleno)-1-pentene.

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