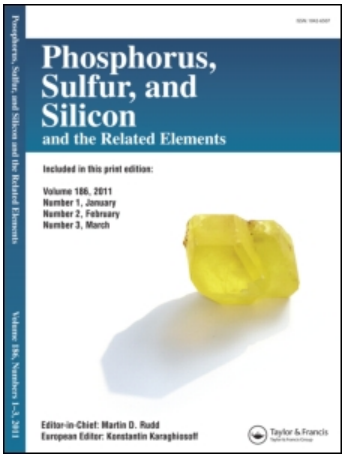

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SELENOL-MEDIATED RADICAL CYCLIZATION OF ENYNES

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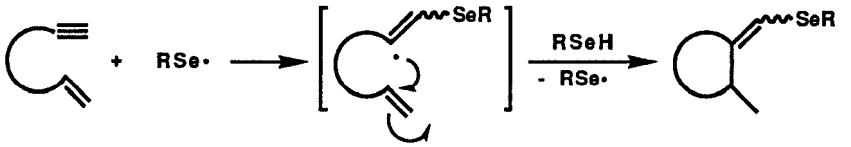
Abstract Intramolecular cyclization of enynes induced by organic seleno radicals has been investigated. Alkaneselenols serve as excellent mediators even under the conditions of fairly high concentration of the substrates, whereas the dilution conditions are essential for the radical cyclization using areneselenols.

INTRODUCTION

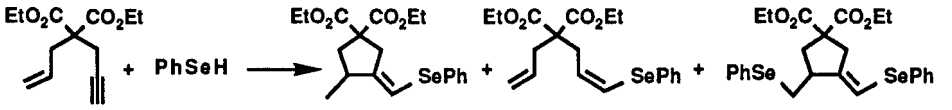
Intramolecular radical cyclization of carbon-carbon unsaturated compounds has proven to be an efficient means for the synthesis of cyclic compounds.[1] For this purpose, a variety of compounds bearing heteroatom-hydrogen bond have been employed as mediators, e.g., tin hydrides,[2] silyl hydrides,[3] and thiols.[4] Although the hydrogen abstraction reaction from organic selenols is accepted as a clean source of seleno radicals,[5] there is no report up to date of selenol-mediated radical cyclization.[6] In this paper, we wish to report the first example of selenol-mediated intramolecular cyclization of enynes.



RESULTS AND DISCUSSION

The radical cyclization of an enyne was performed under several reaction conditions, and the results are summarized in Table I. When the reaction of diethyl propargylallyl-

TABLE I Radical cyclization of an enyne with PhSeH.

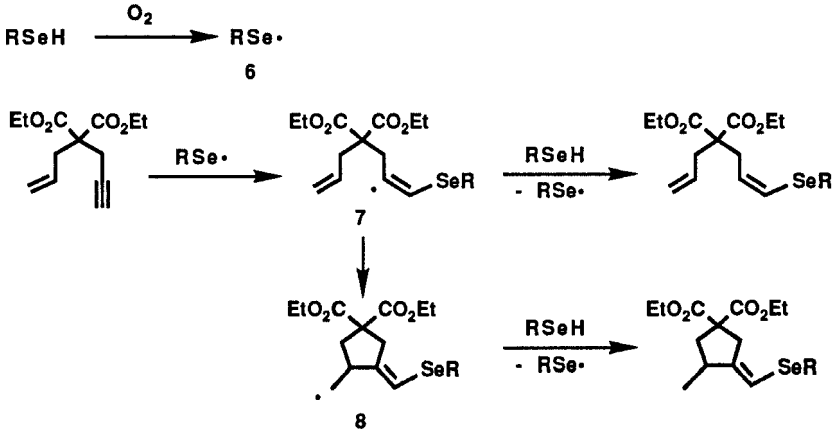


1a 2a 3a 4a 5a

run	initiator	temp./°C	time/h	solvent	yield/% 3a	4a	5a
1	O_2 (air)	70	48	—[a]	6	63	6
2	hν (sunlight)	15	3	—[a]	7	89	4
3[b]	O_2 (air)	110	24	toluene	0	0	0
4[c]	O_2 (air)	110	24	toluene	33	33	33

[a]In the absence of solvent. [b]Diphenyl diselenide and enyne 1a were recovered quantitatively. [c]PhSeH was added dropwise over 5 h.

malonate (**1a**) with 4 equivalents of benzeneselenol (**2a**) without solvent was conducted in the presence of oxygen[7] as the radical initiator, 1,2-addition product **4a** and two types of cyclic products **3a** and **5a** were formed in the ratio of 63/6/6 (run 1). The photo-initiated reaction of enyne **1a** with selenol **2a** in the absence of O_2 resulted in the selective formation of 1,2-adduct **4a** (run 2). These results indicate that, under the condition of high initial concentration of the substrates, the hydrogen abstraction by β-(phenylseleno)alkenyl radical intermediate **7** (R = Ph) from benzeneselenol is much faster than the intramolecular cyclization (see: Scheme I).



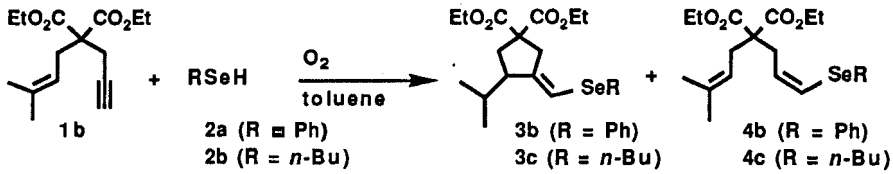
SCHEME I A possible reaction path.

Indeed, it was reported that the rate constants of the hydrogen abstraction from

benzeneselenol and the unimolecular cyclization rate constant for 5-hexenyl radical are 1.7×10^9 M^{-1} s^{-1} (20 °C)[8] and 1×10^5 s^{-1} (25 °C)[9], respectively. Thus, in order to suppress the formation of the 1,2-adduct **4a**, the dilution condition is conceivably required. However, the reaction of enyne **1a** (0.5 mmol) with PhSeH (2 mmol) in toluene (2 mL) gave only diphenyl diselenide, and **1a** was recovered almost quantitatively (run 3). This means that, in such dilution conditions, the coupling reaction of PhSe• to give diphenyl diselenide is much faster than the attack of PhSe• to enyne **1a**. So then, the drop-to-drop addition of benzeneselenol to enyne **1a** (*ca.* 3M) in toluene at 110°C over 20 h was performed, and the cyclization products **3a** and **5a** were successfully produced (run 4). The formation of **5a** is explained by the reaction of cyclopentylmethyl radical **8** (R = Ph) with diphenyl diselenide[6a] formed *in situ* from PhSeH in the presence of O_2.

Table II indicates the results of the radical cyclization of diethyl propargylprenylmalonate (**1b**) using benzeneselenol (**2a**) and *n*-butaneselenol (**2b**). When adding excess PhSeH dropwise to the toluene solution of **1b** at 110°C over 20 h, the cyclization product **3b** was formed in 16 % yield, and 60 % of **1b** was recovered (run 2). The two methyl groups of **1b** may interfere with the attack of PhSe• at the carbon-carbon triple bond. It is expected that the cyclization of enyne **1b** with *n*-butaneselenol proceeds smoothly, because *n*-BuSeH has less hydrogen donating ability toward carbon radicals than PhSeH, and in addition, *n*-butaneseleno radical is more reactive than PhSe• toward carbon-carbon multiple bonds. Gratifyingly, the reaction by just mixing the starting materials (**1b** and *n*-BuSeH) at the initial stage provided the desired cyclic product **3c** in 68 % yield (run 4).

TABLE II **Radical cyclization of an enyne with PhSeH and *n*-BuSeH.**



1b

2a (R = Ph)
2b (R = *n*-Bu)

3b (R = Ph)
3c (R = *n*-Bu)

4b (R = Ph)
4c (R = *n*-Bu)

run	RSeH/eq.		temp./°C	time/h	yield/% 3b or 3c	4b or 4c
1	PhSeH	3.5	70	20	9	15
2	PhSeH	3.5	110	20	16	18
3	*n*-BuSeH	2.0	70	10	38	40
4	*n*-BuSeH	2.0	110	10	68	23

In conclusion, the radical cyclization of enynes by using benzeneselenol took place under the condition of relatively low concentration of benzeneselenol. Contrary to this, *n*-butaneselenol was found to act as a useful mediator for the intramolecular radical cyclization even under the condition of high initial concentration of the substrates. The higher reactivity of *n*-BuSe• (compared with PhSe•) and the lower hydrogen-donating ability of *n*-BuSeH (compared with PhSeH) contribute the efficiency of this radical cyclization of enynes.

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