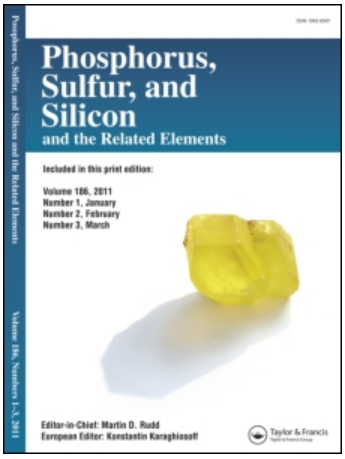


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Highly Selective Thioselenation of Olefins Using Disulfide-Diselenide Mixed System

Akiya Ogawa[a]; Noboru Sonoda[a]
[a] Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka, Japan

To cite this Article Ogawa, Akiya and Sonoda, Noboru(1994) 'Highly Selective Thioselenation of Olefins Using Disulfide-Diselenide Mixed System', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 331 — 332
To link to this Article: DOI: 10.1080/10426509408034224
URL: http://dx.doi.org/10.1080/10426509408034224

Phosphorus, Sulfur, and Silicon, 1994, Vol. 95-96, pp. 331-332
Reprints available directly from the publisher
Photocopying permitted by license only

HIGHLY SELECTIVE THIOSELENATION OF OLEFINS USING DISULFIDE-DISELENIDE MIXED SYSTEM

AKIYA OGAWA and NOBORU SONODA
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

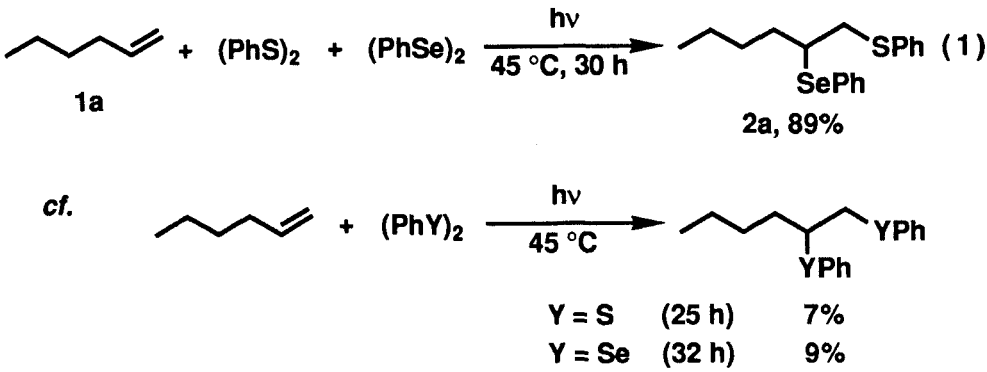
Abstract A highly selective thioselenation of olefins has been attained by using a disulfide-diselenide mixed system.

INTRODUCTION

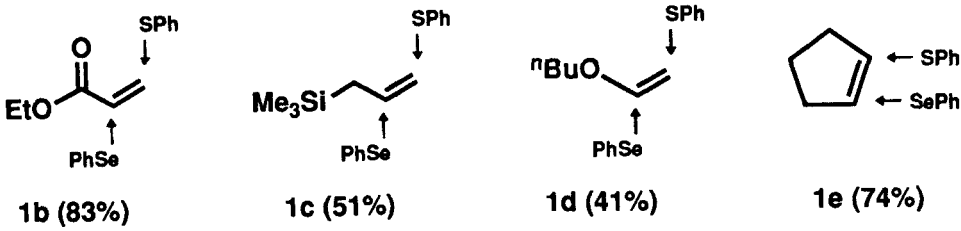
The addition of heteroatom centered radicals to unsaturated compounds is one of the basic reactions in organic chemistry. Organic disulfides and diselenides are known to generate thio and seleno radicals, respectively, upon irradiation with UV or visible light. However, there are no examples reported up to date of the efficient free radical-addition of disulfides and diselenides to olefins. Conceivably, the difficulty in realizing the addition of disulfides to olefins is due to the lower capturing ability of disulfides toward carbon radicals (*i.e.*, $k_{PhSeSePh} / k_{PhSSPh} = 10\sim50$).[1] In contrast, the difficulty of the addition of diselenides may be based on the lower reactivity of seleno radicals toward carbon-carbon double bond (*i.e.*, $k_{PhS\bullet} / k_{PhSe\bullet} = ca.\ 160$).[2] These kinetic data do suggest that, if the addition would be performed in coexistence of $(PhS)_2$ and $(PhSe)_2$, the simultaneous addition of two different heteroatom-groups to olefins may be attained based on the higher reactivity of PhS• toward olefins and the higher capturing ability of $(PhSe)_2$ for carbon radicals.

RESULTS AND DISCUSSION

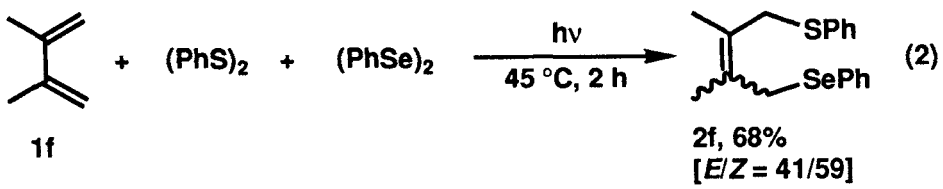
The above considerations prompted us to examine the reaction of 1-hexene (**1a**) with equimolar amounts of $(PhS)_2$ and $(PhSe)_2$ by irradiation through Pyrex with a tungsten lamp at 45 °C for 30 h, which successfully provided 1-(phenylthio)-2-(phenylseleno)-hexane (**2a**) as a sole product (Eq. 1).[3] Similar conditions can be employed with a variety of olefins such as **1b~1e**. The thioselenation of terminal olefins proceeded regioselectively. Cyclopentene underwent thioselenation stereoselectively to give the



corresponding *E*-adducts. Noteworthy is that some side-reactions, which may occur under radical conditions (*e.g.*, dimerization of alkyl radicals and polymerization of olefins), were completely suppressed in the presence of $(PhSe)_2$.



An application of this thioselenation to conjugated dienes was examined: Upon irradiation with a tungsten lamp for 2 h, the reaction of 2,3-dimethyl-1,3-butadiene (**1f**) with stoichiometric amounts of $(PhS)_2$ and $(PhSe)_2$ produced 1,4-adduct (**2f**) in good yield (Eq. 2).



REFERENCES

1. O. Ito, J. Am. Chem. Soc., 105, 850 (1983).
2. G. A. Russell and H. Tashtoush, J. Am. Chem. Soc., 105, 1398 (1983).
3. A. Ogawa, H. Tanaka, H. Yokoyama, R. Obayashi, K. Yokoyama, and N. Sonoda, J. Org. Chem., 57, 111 (1992).