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Diphenyl Diselenide-Assisted Dithiolation of 1,3-Dienes with Diphenyl Disulfide upon Irradiation with Near-UV Light

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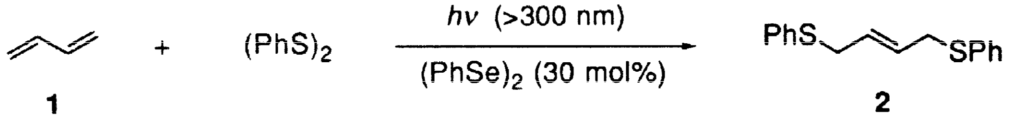
Abstract: *While the photoinduced reaction of 1,3-dienes with diphenyl disulfide provides a polymeric mixture, the same reaction in the presence of a catalytic amount of diphenyl diselenide provides the corresponding 1,4-dithiolation products (2) selectively in good yields. The higher carbon radical capturing ability of $(PhSe)_2$ and the reversibility of allylic selenides under photoirradiation contribute to the high efficiency of the conjugate addition of $(PhS)_2$ to 1,3-dienes under radical conditions.*

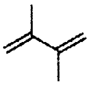
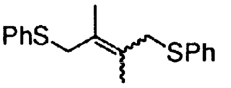
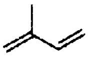
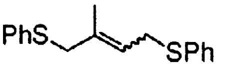
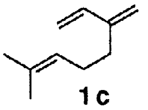
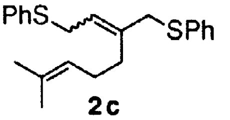
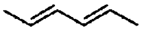
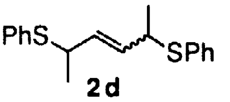
It is well-established that the absorption maximum of organic disulfides lies in the ultraviolet region; therefore, irradiation with UV or near-UV causes homolytic cleavage of the sulfur-sulfur bond generating thiyl radicals as label intermediates.[1] Thus, if the photolysis of disulfides is performed in the presence of 1,3-dienes, the conjugate addition reaction may take place giving 1,4-dithiolation products. However, the photoinduced reaction of disulfides with 1,3-dienes afforded a polymeric mixture mainly (*e.g.*, the reaction of $(PhS)_2$ to 2,3-dimethyl-1,3-butadiene (**1a**) yielded 20% of 1,4-adduct (**2a**) with a complex polymeric mixture). This is most probably due to the poor capturing ability of disulfides toward carbon radicals.[2] Herein we report that a novel radical addition of $(PhS)_2$ to 1,3-dienes proceeds successfully in the co-presence of a catalytic amount of its selenium analogue, *i.e.*, $(PhSe)_2$ (eq 1).



(1)

Upon irradiation with a tungsten lamp (500 W) through Pyrex, the reaction of 1,3-diene (**1a**, 0.5 mmol) with $(PhS)_2$ (1 mmol) was conducted at 45 °C for 10 h in the presence of $(PhSe)_2$ (30 mol%), which provided 1,4-bis(phenylthio)-2,3-dimethyl-2-butene (**2a**) in 90% yield after purification by preparative TLC on silica gel (hexane) (entry 1 in Table 1).[3] Similar conditions can be employed with isoprene (**1b**) and β-myrcene (**1c**), providing the corresponding conjugate addition products (**2b**[4] and **2c**) selectively (entries 2,3). In the case of 2,4-hexadiene (**1d**) as an internal diene, longer reaction time was essential and the yield of the 1,4-adduct (**2d**) increased when

Table 1. $(PhSe)_2$-Catalyzed Dithiolation of 1,3-Diene with $(PhS)_2$[a]

Entry	Substrate	Time, h	Product	Yield, %[b]	*E/Z*
1	 **1a**	10	 **2a**	90	39/61
2	 **1b**	30	 **2b**	77	25/75
3	 **1c**	13	 **2c**	85	41/59
4	 **1d**	107[c]	 **2d**	57	50/50

[a] Reaction conditions: diene (0.5 mmol), $(PhS)_2$ (1 mmol), $(PhSe)_2$ (0.15 mmol), 45 °C, $CDCl_3$ (0.5 mL), *hν*: tungsten lamp (500 W, Pyrex). [b] Isolated yield. [c] $(PhSe)_2$ (0.5 mmol)

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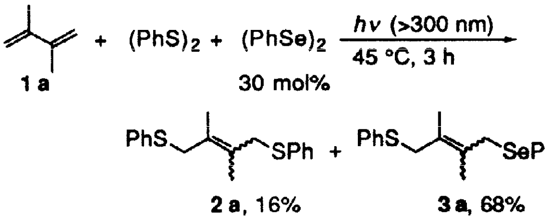
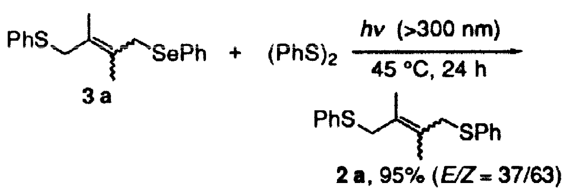
one equivalent of $(PhSe)_2$ was used (entry 4) (*cf.* 33% of **2d** was obtained when 30 mol% of $(PhSe)_2$ was used). On the other hand, 1,1,4,4-tetra(alkyl)-substituted 1,3-dienes like 2,5-dimethyl-2,4-hexadiene and 1,4-diaryl-substituted 1,3-dienes like 1,4-diphenyl-1,3-butadiene did not undergo radical dithiolation with $(PhS)_2$ even in the presence of one equivalent of $(PhSe)_2$. This is most probably due to the steric hindrance by the terminal substituents and partly due to the instability of benzylic chalcogenides under photoirradiation conditions.

To gain insight into the reaction pathway, the reaction of **1a** with $(PhS)_2$ in the presence of 30 mol% of $(PhSe)_2$ was followed by taking the ^{1}H NMR spectra. At the initial stage, the reaction involved the formation of the thioselenating adduct (**3a**) as a kinetic product, as exemplified in eq 2.[5] The yield of **2a** increased with the lapse of time and the yield of **3a** decreased. Furthermore, the photoirradiated reaction of isolated **3a** with $(PhS)_2$ at 45 °C for 24 h gave rise to **2a** in 95% yield (eq 3). These results strongly suggest reversibility whereby the allylic selenide **3a** regenerates the allylic radical under photoirradiation conditions.



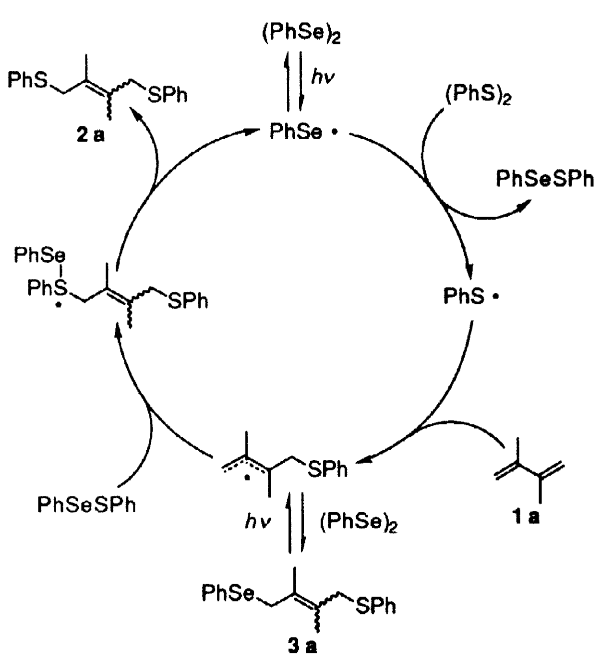
(2)



(3)

A possible catalytic cycle is shown in Scheme 1. Since the absorption of $(PhSe)_2$ is larger than that of $(PhS)_2$ in the near-UV and visible region, the homolytic cleavage of $(PhSe)_2$ takes place preferentially to form PhSe•, which can not add to 1,3-dienes owing to its lower reactivity.[6] The S$_H$2 reaction of PhSe• with $(PhS)_2$ leads to PhS• and seleno sulfide (PhSeSPh).[5] The addition of PhS• to **1a** generates an allylic radical, which is in equilibrium with the thioselenating adduct (**3a**) under photoirradiated conditions. The subsequent S$_H$2 reaction of the allylic radical with the seleno sulfide produces a thermodynamically more stable dithiolation product (**2a**) with regeneration of PhSe•. In the catalytic reaction, $(PhSe)_2$ (which has excellent carbon radical capturing ability) inhibits the polymerization of dienes.

In summary, a novel $(PhSe)_2$-catalyzed addition of $(PhS)_2$ to 1,3-dienes has been revealed. Further investigation along these lines is now in progress.



Scheme 1. A Possible Reaction Path

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References and Notes

1. Schmidt, U.; Müller, A.; Markau, K. *Chem. Ber.* **1964**, *97*, 405.
2. The rate constants for the S$_H$2 reaction of 5-hexenyl radical with $(PhS)_2$ and $(PhSe)_2$ are 7.6 x 10^4 M^{-1} s^{-1} and 1.2 x 10^7 M^{-1} s^{-1}, respectively. See: Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398.
3. **2a**: a yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) [*E*-**2a**] δ 1.78 (s, 6H), 3.34 (s, 4H), 7.16-7.53 (m, 10H). [*Z*-**2a**] δ 1.66 (s, 6H), 3.51 (s, 4H), 7.15-7.33 (m, 10H); ^{13}C NMR (68 MHz, $CDCl_3$) [*E*-**2a**] δ 18.52, 38.62, 126.49, 128.72, 129.81, 130.66, 136.62. [Z-**2a**] δ 17.87, 39.47, 126.47, 128.74, 129.88, 130.83, 136.55; IR (NaCl) 3056, 2917, 1584, 1479, 1438, 737, 690 cm^{-1}; MS (EI), *m/z* = 300 (M^+, 1.1); Anal. Calcd for $C_{18}H_{20}S_2$: C, 71.90; H, 6.71. Found: C, 72.18; H, 7.01.
4. **2b**: ^{1}H NMR [*E*-**2b**] δ 1.84 (s, 3H), 3.26 (d, 2H, *J* = 7.8 Hz), 3.40 (s, 2H), 5.40 (t like, 1H), 7.18-7.37 (m, 10H). [Z-**2b**] δ 1.69 (s, 3H), 3.48 (s, 2H), 3.48 (d, 2H, *J* = 7.3 Hz), 5.40 (t like, 1H), 7.18-7.37 (m, 10H); ^{13}C NMR [*E*-**2b**] δ 22.77, 31.71, 36.41, 123.74, 126.20, 126.84, 128.75, 128.81, 129.88, 131.26, 134.83, 136.06, 136.23. [*Z*-**2b**] δ 15.29, 32.19, 43.87, 123.50, 126.14, 126.31, 128.71, 128.71, 129.95, 130.36, 134.74, 136.06, 136.18; IR (NaCl) 3057, 2913, 1583, 1480, 1438, 738, 690 cm^{-1}; MS (EI), *m/z* = 286 (M^+, 0.6); exact mass (M^+) calcd for $C_{17}H_{18}S_2$ 286.0816, found 286.0833.
5. Ogawa, A.; Tanaka, H.; Yokoyama, H.; Obayashi, R.; Yokoyama, K.; Sonoda, N. *J. Org. Chem.* **1992**, *57*, 111.
6. The addition rate constants to styrene: $k_{PhS\bullet}$ = 5.1 x 10^7 $M^{-1}s^{-1}$; $k_{PhSe\bullet}$ = 2.2 x 10^6 $M^{-1}s^{-1}$: Ito, O. *J. Am. Chem. Soc.* **1983**, *105*, 850.