- $COCH_3$) 384.2539 found 384.2538.

Registry No. 1, 51493-69-7; 2, 133349-39-0; 2 (18-acid), 135615-57-5; 3, 133372-88-0; 3 (acid), 135615-59-7; 3 (*N*-(1,1-dimethyl-2-hydroxyethyl)amide), 135615-58-6; 6, 135615-46-2; 7, 135615-47-3; 8, 135615-48-4; 8 (debenzylated 18-aldehyde), 133349-48-1; 9, 135615-49-5; 10, 135615-50-8; 11, 135615-51-9; 11 (17-alcohol), 135615-60-0; 11 (17-TBDMS ether), 135615-61-1; 12, 135615-52-0; 13, 135615-53-1; 14, 135615-54-2; 15, 135615-55-3; 15 (17-alcohol), 135615-62-2; 16, 135615-56-4.

Supplementary Material Available: Copies of ^{1}H NMR spectra for compounds **3**, **6-8**, **10-16**, and unnumbered intermediates and ^{13}C NMR spectra for compounds **8**, **10**, **13**, **15**, and **16** (23 pages). Ordering information is given on any current masthead page.

Photoinitiated Addition of Diphenyl Diselenide to Acetylenes[1]

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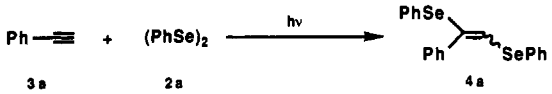
The addition to unsaturated compounds of heteroatom-centered radicals formed by the homolytic dissociation of a heteroatom–heteroatom bond is one of the most basic reactions in organic chemistry.[2] It is well known that, under UV irradiation, disulfides add to terminal alkynes via a radical chain mechanism.[3] However, similar additions of diselenides to acetylenes have not been reported except in cases where electron-deficient acetylenes like dimethyl acetylenedicarboxylate and methyl propiolate were reactants.[4] For example, the difficulty in realizing the addition of diphenyl diselenide to acetylenes is mainly due to the lower reactivity of the phenylseleno radical (**1**), compared to the phenylthio radical,[5] toward carbon–carbon multiple bonds and the tendency of phenylseleno radical to combine to re-form the starting diselenide, which results in a low concentration of **1** in the system.

Results and Discussion

The presence of high initial concentrations of acetylene and diphenyl diselenide and the use of an efficient means of generating the phenylseleno radical (**1**) are believed to be critical to the success of the addition. Thus, three factors were examined: (a) the light source, (b) the initial concentrations of the reactants, and (c) the reaction temperature. With regard to (a), near ultraviolet light (λ = 300–400 nm) was expected to be most suitable for the efficient generation of **1**, because diphenyl diselenide (**2a**) exhibits its absorption maximum in the near ultraviolet ($\lambda_{\max}$ = 330 nm, $\epsilon_{\max} = 10^3$).[5] Thus, upon irradiation with monochromatic UV light (365 nm), the addition of **2a** to phenylacetylene (**3a**) proceeded with high efficiency (entry 1, Table I). Sunlight was also effective (entry 2). However, upon irradiation with UV light, the yield of the 1,2-adduct **4a** decreased and elemental selenium was deposited. Addition did not take place in the dark (entry 3). It was convenient to irradiate with a tungsten lamp through a Pyrex (entry 4), so this was done routinely.

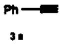
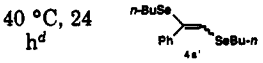
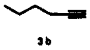
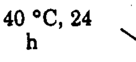
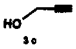
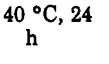
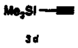
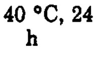
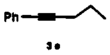
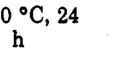
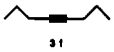
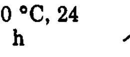
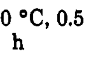
Table I. Addition of Diphenyl Diselenide to Phenylacetylene[a]



entry	radiation	solvent	T (°C)	time (h)	yield (%)	E/Z
1	$h\nu$ (λ = 365 nm)	$CDCl_3$	25	10	80	86/14
2	sunlight (through Pyrex)	*b*	25	3	83	82/18
3	dark	*b*	40	24	c	
4	tungsten lamp (500 W, through Pyrex)	*b*	40	4	93	83/17

[a] Phenylacetylene (1 mmol), $(PhSe)_2$ (1 mmol). [b] In the absence of solvent. [c] No reaction.

Table II. Photoinitiated Addition of Diphenyl Diselenide to Acetylenes[a]

entry	substrate	conditions	product	yield (%)[b]	E/Z[c]
1	 3a	40 °C, 24 h[d]	 4a'	83	82/18
2	 3b	40 °C, 24 h	 4b	91 (100)	95/5
3	 3c	40 °C, 24 h	 4c	81 (93)	73/27
4	 3d	40 °C, 24 h	 4d	73 (89)	28/72
4	 3e	40 °C, 24 h	 4e	69 (81)	95/5
6	 3f	70 °C, 24 h	 4f	18 (22)	90/10
7	 3g	40 °C, 0.5 h	 4g	87 (98)	17/83

[a] Acetylene (1 mmol), $(PhSe)_2$ (1 mmol), $h\nu$ (tungsten lamp, 500 W, Pyrex), no solvent. [b] Isolated yield (NMR yield). [c] The E/Z ratio was determined by ^{1}H NMR. [d] $(n\text{-}BuSe)_2$ (1 mmol) was used.

As to (b), reaction in the absence of solvent gave optimum results. In contrast, in the presence of solvent, longer reaction times were required to give high yields of product. As to (c), temperatures above 40 °C favored addition in the absence of solvent, because the diphenyl diselenide (mp 63 °C)/acetylene mixture becomes homogeneous above that temperature.

Representative results are shown in Table II. Quite high yields were obtained from a variety of acetylenes.[6] The sterochemistry of the adducts was determined from the results of NOE experiments[7] and the respective ^{77}Se NMR spectra.[8] The simple acetylenes **3a**, **3b**, **3c**, **3e**, and **3f** preferentially afforded the (*E*)-bis(phenylseleno)olefins **4a**, **4b**, **4c**, **4e**, and **4f**, respectively, whereas silylacetylene

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(1) This work was first presented at the 56th Annual Meeting of Chemical Society of Japan, 1988 (April 4th).

(2) Kochi, J. K. *Free Radicals*; Wiley: New York, 1973; Vol. II.

(3) Heiba, E. I.; Dessau, R. M. *J. Org. Chem.* **1967**, *32*, 3837.

(4) Back, T. G.; Krishna, M. V. *J. Org. Chem.* **1988**, *53*, 2533.

(5) It was reported that the rate constants for the addition of $\mathrm{PhSe}^\bullet$ to some vinyl monomers are smaller than those of $\mathrm{PhS}^\bullet$ by a factor of ~10–50. See: Ito, O. *J. Am. Chem. Soc.* **1983**, *105*, 850.

(6) The addition to such activated acetylenes as conjugated enyne **3g** was complete within 0.5 h, whereas longer reaction times were required for unactivated acetylenes (e.g., **3b**, **3c**, **3d**, **3e**, and **3f**).

(7) The stereochemistry was established unambiguously by an NOE experiment in which the vinyl singlet was enhanced upon irradiation of the signal due to the protons of the allylic methylene group.

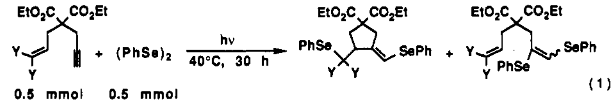
(8) It is known that $J_{\mathrm{Se-Se}}$ of *vic*-bis(phenylseleno)olefins is in the range 2–25 Hz for *E* isomers and 77–117 Hz for *Z* isomers. See: (a) Johannsen, I.; Eggert, H. *J. Am. Chem. Soc.* **1984**, *106*, 1240. (b) Johannsen, I.; Henriksen, L.; Eggert, H. *J. Org. Chem.* **1986**, *51*, 1657.

0022-3263/91/1956-5721$02.50/0 © 1991 American Chemical Society

3d gave (*Z*)-**4d** as the major product.[9] Enyne **3g** chemoselectively underwent addition to the triple bond. Dialkyl diselenides like dibutyl diselenide (**2b**) also added to acetylenes.[10]

The reaction of diselenide **2a** with phenylacetylene (**3a**) was performed in the dark in the presence of benzeneselenol (**5**), which served as the source of the phenylseleno radical (**1**), to gain evidence that the addition indeed proceeded via a radical chain pathway. It was reported that **5** reacts with molecular oxygen to give **1**.[11] Thus, selenol **5** (2 mmol, 0.33 equiv) was added drop-by-drop to a CCl_4 (1 mL) solution of **2a** (6 mmol) and phenylacetylene (**3a**, 6 mmol) in the dark under an atmosphere of oxygen (Scheme I). A mixture of the diselenide adduct **4a** (3.2 mmol) and the selenol adduct **6** (0.9 mmol) was formed. This result supports the hypothesis that the addition proceeds by a radical chain mechanism that involves the formation of an alkenyl radical intermediate (**7**) by the addition of the phenylseleno radical (**1**) to the acetylene. Subsequent S_H2 attack by **7** on diphenyl diselenide (**2a**) leads to the formation of 1,2-bis(phenylseleno)olefin **4** and the regeneration of **1**.

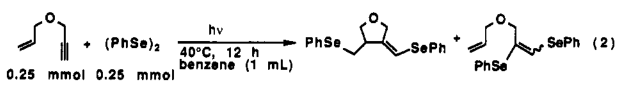
That this photoinitiated reaction of diselenides and acetylenes could be applied to the radical cyclization of olefins was demonstrated by using acetylenes bearing a carbon–carbon double bond at a suitable position.[12] Thus, when irradiated through Pyrex by a tungsten lamp at 40 °C in the absence of solvent, enyne **3h** and **2a** provided a single five-membered cyclic stereoisomer (**4h′**, 53%) along with the 1,2-addition product **4h** (29%) (eq 1). The yield of **4h′** increased when benzene was used as the solvent (**4h′**, 70%; **4h**, 8%). On the other hand, it is of interest to note that the reaction of enyne **3i** gave a high yield of cyclic product in the absence of solvent. No six-membered cyclic product was detected. Under similar conditions, the propargyl vinyl ether (**3j**) also cyclized to a single stereoisomer, **4j** (eq 2).



(1)

enyne	solvent	product: yield[a]	
3h (Y = H)	no solvent	4h′: 53 %	4h: 29 %
	benzene (1 mL)[b]	4h′: 70 % (77 %)	4h: 8 % (9 %)
3i (Y = Me)	no solvent	4i′: (84 %)	4i: (16 %)

[a] Isolated yield (NMR yield). [b] Time: 19 h.



(2)

Experimental Section

Unless otherwise noted, materials were obtained commercially and were purified by distillation. Diphenyl diselenide (**2a**) was prepared according to the literature[13] and was recrystallized from *n*-hexane. Dibutyl diselenide (**2b**) was synthesized by the air-oxidation of the product of the reaction of *n*-butyllithium with an equimolar amount of metallic Se. Compound **2b** was purified by column chromatography on silica gel (*n*-hexane). Benzeneselenol (**5**) was prepared by methanolysis of phenyl trimethylsilyl selenide and was purified by distillation immediately before use.[14] Enynes **3h–j** were synthesized by literature methods[15] and were purified by distillation.

The purity of all the compounds described (except (*Z*)-**4a′**, (*Z*)-**4e**, and (*Z*)-**4f**[16]) was judged to be >95% by ^{13}C and ^1H NMR analysis.

^1H NMR spectra of $CDCl_3$ solutions were recorded with JEOL JNM-GSX-270 (270 MHz) and JNM-GSX-400 (400 MHz) spectrometers. Me_4Si served as the internal standard. ^{13}C and ^{77}Se NMR spectra of $CDCl_3$ solutions were recorded with a JEOL JNM-GSX-270. Chemical shifts in the ^{13}C NMR spectra were determined relative to $CDCl_3$ but are reported in ppm downfield from Me_4Si (δ_{CDCl_3} = 76.9 ppm). Chemical shifts in the ^{77}Se NMR spectra were determined relative to external Me_2Se. IR spectra were recorded with a Perkin-Elmer Model 1600 spectrometer. Mass spectra were recorded with a JEOL JMS-DX303 spectrophotometer. Elemental analyses were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University.

General Procedure for the Photoinitated Addition of Diphenyl Diselenide to Acetylenes. The reaction of 1-hexyne (**3b**) and diphenyl diselenide (**2a**) is typical. In a Pyrex glass tube, were placed 1-hexyne (**3b**) (1 mmol) and diphenyl diselenide (**2a**) (1 mmol). The tube was filled with Ar and was sealed under reduced pressure. The mixture was irradiated at 40 °C for 24 h with a tungsten lamp (500 W) positioned approximately 20 cm from the tube. The mixture was purified by flash chromatography on silica gel (*n*-hexane) to provide 359 mg (91%) of a 95:5 mixture of (*E*)- and (*Z*)-1,2-bis(phenylseleno)-1-hexene (**4b**, a pale yellow oil). The two isomers were separated by preparative TLC on silica gel (*n*-hexane). ***E* isomer:** ^1H NMR (270 MHz, $CDCl_3$) δ 0.90 (t, 3 H, *J* = 6.8 Hz), 1.34 (m, 2 H), 1.54 (m, 2 H), 2.43 (t, 2 H, *J* = 6.8 Hz), 6.71 (s, 1 H), 7.24–7.29 (m, 6 H), 7.41 (m, 2 H), 7.52 (m, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.93, 22.17, 30.65, 36.05, 122.15 (=*C*H), 127.00 (p), 127.67 (p), 129.22 (m), 129.25 (m), 129.89 (ipso), 131.10 (ipso), 131.46 (o), 133.50 (o), 135.62 (=*C*); ^{77}Se NMR (51.5 MHz, $CDCl_3$) δ 368.93 (J_{Se-Se} = 18.7 Hz), 454.87 (J_{Se-Se} = 18.7 Hz); IR (NaCl) 3065, 2920, 1580, 1485, 1448, 1070, 1028, 738, 691 cm^{-1}; MS (EI) *m/e* = 396 (M^+, 37). Anal. Calcd for $C_{18}H_{20}Se_2$: C, 54.83; H, 5.11. Found: C, 54.45; H, 5.11. ***Z* isomer:** ^1H NMR (270 MHz, $CDCl_3$) δ 0.81 (t, 3 H, *J* = 6.8 Hz), 1.22 (m, 2 H), 1.46 (m, 2 H), 2.27 (t, 2 H, *J* = 6.8 Hz), 6.92 (s, 1 H), 7.26–7.29 (m, 6 H), 7.50–7.57 (m, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.78, 21.83, 31.05, 39.61, 127.25 (p), 127.33 (p), 127.91 (=*C*H), 129.14 (m), 129.24 (m), 129.47 (ipso), 131.19 (ipso), 132.60 (o), 132.84 (o), 136.25 (=*C*); IR (NaCl) 3055, 2954, 1577, 1475, 1437, 1229, 1069, 1021, 734, 690 cm^{-1}; MS (EI) *m/e* = 396 (M^+, 100). Anal. Calcd for $C_{18}H_{20}Se_2$: C, 54.83; H, 5.11. Found: C, 54.94; H, 5.39. NOE experiment: irradiation of the C-3 methylene triplet at δ 2.27 resulted in a 15% enhancement of the signal at δ 6.92 (vinyl singlet).

Reaction of Phenylacetylene (3a) with Diphenyl Diselenide (2a) in the Presence of Benzeneselenol (5) and O_2. To a mixture of phenylacetylene (6 mmol), diphenyl diselenide (6 mmol), and carbon tetrachoride (1 mL) under an atmosphere of O_2 was added benzeneselenol (2 mmol) dissolved in CCl_4 (5 mL) drop-to-drop at 25 °C over 1 h in the dark. After 1 h of stirring, the solvent was evaporated in vacuo. Purification of the residue by column chromatography on silica gel (*n*-hexane) provided 0.9 mmol of 2-(phenylseleno)styrene (**6**) and 3.2 mmol of bis(phenylseleno)styrene (**4a**, a pale yellow oil). ***E* isomer:** ^1H NMR (270 MHz, $CDCl_3$) δ 7.07 (s, 1 H), 7.20–7.49 (m, 15 H); ^{13}C

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[9] In the case of the adducts **4c**, **4d**, and **4g**, *E* to *Z* isomerization was observed upon tungsten lamp irradiation. In contrast, the adducts of simple alkynes like **3b** did not isomerize.

[10] The addition of dibutyl diselenide to unactivated acetylenes like **3b** required longer reaction times (37% yield after 120 h).

[11] (a) Masawaki, T.; Uchida, Y.; Ogawa, A.; Kambe, N.; Miyoshi, N.; Sonoda, N. *J. Phys. Org. Chem.* **1988**, *1*, 115. (b) Masawaki, T.; Ogawa, A.; Kambe, N.; Murai, S.; Sonoda, N. *J. Phys. Org. Chem.* **1988**, *1*, 119. (c) Masawaki, T.; Ogawa, A.; Kambe, N.; Ryu, I.; Sonoda, N. *Chem. Lett.* **1987**, 2407.

[12] For the tin hydride promoted radical cyclization of enynes, see, for example: (a) Stork, G.; Mook, R., Jr. *Tetrahedron Lett.* **1986**, *27*, 4529. (b) Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 2829. (c) Beckwith, A. L. J.; O'Shea, D. M. *Tetrahedron Lett.* **1986**, *27*, 4525. (d) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547.

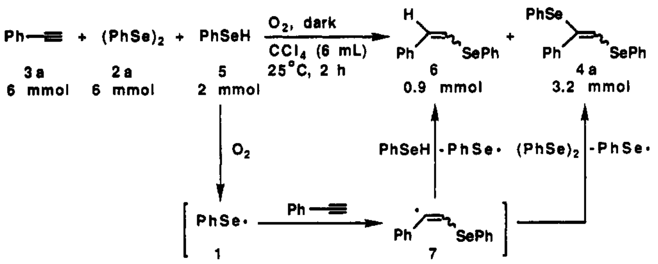
[13] Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.

[14] Miyoshi, N.; Ishii, H.; Kondo, K.; Murai, S.; Sonoda, N. *Synthesis* **1979**, 300.

[15] For the synthesis of **3h** and **3i**, see: (a) Grigg, R.; Stevenson, P.; Worakun, T. *Tetrahedron* **1988**, *44*, 4967. For the synthesis of **3j**, see: (b) Billington, D. C.; Willison, D. *Tetrahedron Lett.* **1984**, *25*, 4041.

[16] Adducts (*Z*)-**4e** and (*Z*)-**4f** could not be isolated in pure form because they were formed in low yield (<4% by ^1H NMR). In the case of (*Z*)-**4a′**, the *Z* isomer could not be completely separated from the *E* isomer.

Scheme I



NMR (68 MHz, $CDCl_3$) δ 125.99 (p), 127.37 (p), 127.41 (p), 128.23 (m and =*C*H), 128.60 (o), 129.13 (m), 129.22 (m), 130.51 (ipso), 130.65 (ipso), 131.16 (ipso), 132.06 (o), 133.03 (o), 139.54 (=*C*); ^{77}Se NMR (51.5 MHz, $CDCl_3$) δ 406.35 (J_{Se-Se} = 27.6 Hz), 508.94 (J_{Se-Se} = 27.6 Hz); IR (NaCl) 3052, 1576, 1475, 1438, 1070, 1021, 736, 689 cm^{-1}; MS (EI) *m*/*e* = 416 (M^+, 71). Anal. Calcd for $C_{20}H_{16}Se_2$: C, 57.99; H, 3.89. Found: C, 57.71; H, 4.07. ***Z* isomer**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.06–7.57 (m, 16 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 126.61 (p), 127.27 (m), 127.49 (p), 127.84 (p), 128.26 (m), 129.09 (m), 129.38 (o), 130.33 (ipso), 130.86 (o), 131.00 (ipso), 131.49 (ipso), 133.20 (o), 136.04 (=*C*H), 140.52 (=*C*); ^{77}Se NMR (51.5 MHz, $CDCl_3$) δ 390.11 (J_{Se-Se} = 80 Hz), 436.35 (J_{Se-Se} = 80 Hz); IR (NaCl) 3055, 1577, 1476, 1438, 1022, 733, 690 cm^{-1}; MS (EI) *m*/*e* = 416 (M^+, 71). Anal. Calcd for $C_{20}H_{16}Se_2$: C, 57.99; H, 3.89. Found: C, 58.07; H, 4.05.

Radical Cyclization of Enyne 3h Induced by the Phenylseleno Radical. In a Pyrex glass tube were placed enyne **3h** (0.5 mmol), diphenyl diselenide **2a** (0.5 mmol), and benzene (1 mL). The tube was sealed under reduced pressure. The mixture was irradiated with a tungsten lamp (500 W). The solvent was then evaporated in vacuo. The residue was purified by preparative TLC on silica gel (*n*-hexane/Et_2O, 10:1) to provide 197 mg (70%) of cyclic **4h′** along with 22 mg (8%) of the adduct **4h**. **4h′**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.21 (t, 3 H, *J* = 7.0 Hz), 1.24 (t, 3 H, *J* = 7.0 Hz), 2.11 (dd, 1 H, *J* = 9.5, 13.1 Hz), 2.78 (dd, 1 H, *J* = 5.8, 11.9 Hz), 2.87–3.22 (m, 5 H), 4.17 (q, 2 H, *J* = 7.0 Hz), 4.19 (q, 2 H, *J* = 7.0 Hz), 6.33 (s, 1 H), 7.22–7.29 (m, 6 H), 7.41–7.51 (m, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.92 (OCH_2CH_3), 13.96 (OCH_2CH_3), 32.05 (J_{C-Se} = 32.4 Hz, CH_2SePh), 40.26, 40.45, 43.96, 58.16 (O=C*C*C=O), 61.58 (OCH_2CH_3), 61.61 (OCH_2CH_3), 112.10 (C=*C*H), 126.80 (p), 127.02 (p), 129.03 (m), 129.13 (m), 129.98 (ipso), 131.08 (ipso), 131.82 (o), 132.92 (o), 147.43 (*C*=CH), 171.13 (C=O), 171.23 (C=O); IR (NaCl) 3056, 2980, 2933, 1731, 1578, 1477, 1438, 1250, 1179, 1022, 737, 691 cm^{-1}; MS (EI) *m*/*e* = 552 (M^+, 0.6). Anal. Calcd for $C_{25}H_{28}O_4Se_2$: C, 54.60; H, 5.13. Found: C, 54.46; H, 5.46.

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Registry No. **2a**, 1666-13-3; **3a**, 536-74-3; **3b**, 693-02-7; **3c**, 107-19-7; **3d**, 1066-54-2; **3e**, 4250-81-1; **3f**, 1942-45-6; **3g**, 78-80-8; **3h**, 101268-55-7; **3i**, 133788-02-0; **3j**, 51580-41-7; (*E*)-**4a**, 132330-37-1; (*Z*)-**4a**, 7392-13-4; (*E*)-**4a′**, 134904-95-3; (*Z*)-**4a′**, 134904-96-4; (*E*)-**4b**, 134904-97-5; (*Z*)-**4b**, 101349-67-1; (*E*)-**4c**, 134904-98-6; (*Z*)-**4c**, 134904-99-7; (*E*)-**4d**, 134905-00-3; (*Z*)-**4d**, 134905-01-4; (*E*)-**4e**, 134905-02-5; (*Z*)-**4e**, 134905-03-6; (*E*)-**4f**, 134905-04-7; (*Z*)-**4f**, 134905-05-8; (*E*)-**4g**, 134905-06-9; (*Z*)-**4g**, 134905-07-0; **4h**, 134905-09-2; **4h′**, 134905-08-1; **4i**, 134905-11-6; **4i′**, 134905-10-5; **4j**, 134905-13-8; **4j′**, 134905-12-7; **6**, 96983-85-6; (*n*-BuSe)$_2$, 20333-40-8.

Supplementary Material Available: Analytical data on the compounds prepared (IR, ^{1}H NMR, ^{13}C NMR, and mass spectra; elemental analyses) (12 pages). Ordering information is given on any current masthead page.

Regiospecific Ortho Lithiation of *o*-Halophenyl *p*-Tolyl Sulfoxides and Synthesis of Meta-Substituted Optically Active Aryl Alcohols

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The regiospecific introduction of substituents onto aromatic rings has been an important objective in synthetic organic chemistry. Electrophilic substitution is one of the common procedures to give various substituted aromatic compounds, but this method is not suited to some substitution patterns.[1] Recently, regiospecifically directed metalation of aromatic rings has attracted attention, and many functional groups that orient the lithiation to the ortho position of the aromatic ring have been reported.[2] During studies on the lithiation reactions of pyridyl sulfoxides, we found that regiospecific ortho lithiation of aryl pyridyl sulfoxides afforded the corresponding aryl ortho-substituted pyridyl sulfoxides in moderate yields.[3] In this note, we report a new ortho-lithiation reaction of diaryl sulfoxides that allows the arylsulfinyl group to be easily removed after introduction of enantiomerically enriched alcohol groups onto the benzene ring with optically active sulfoxides.

Results and Discussion

When diphenyl sulfoxide was allowed to react with lithium diisopropylamide (LDA) at −78 °C in THF and subsequently with acetaldehyde, 2-(1-hydroxyethyl)phenyl phenyl sulfoxide was obtained in 60% yield, which was found to be a mixture of two diastereomers in the ratio of 63:37. However, similar treatment of phenyl *p*-tolyl sulfoxide with LDA and acetaldehyde gave mixtures of three sulfoxides, one of which was found to be alkylated at the ortho position of phenyl group, another at the ortho position of *p*-tolyl group, and the other at the methyl group of *p*-tolyl group. In the course of further studies on the regiospecific lithiation of diaryl sulfoxides and also asymmetric induction in the reactions of the lithiated intermediates with aldehydes, *o*-halophenyl *p*-tolyl sulfoxides (**1a**, X = Cl; **1b**, X = Br; **1c**, X = I) together with optically active sulfoxides (*S*)-(−)-**1a** and (*S*)-(−)-**1b** were synthesized.[4] When the sulfoxides **1a–c** were treated with organolithium reagents and then with acetaldehyde, the products changed dramatically depending on the sulfoxide and organolithium reagents employed. Namely, the sulfoxide **1a** gave solely the sulfinyl transfer product **4**, which was racemized completely, while the sulfoxide **1b** gave a

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(1) (a) Norman, R. O. C.; Taylor, R. *Electrophilic Substitution in Benzenoid Compounds*; Elsevier: Amsterdam, 1965. (b) Olah, G. A. *Friedels-Crafts and Related Reaction*; Interscience: New York, 1963. (c) Pearson, D. E.; Buehler, C. A. *Synthesis* **1972**, 533. (d) Effenberger, F. *Ibid.* **1980**, 151.

(2) (a) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879. (b) Katritzky, A. R.; Lue, P. *J. Org. Chem.* **1990**, *55*, 74. (c) Negishi, E.; Zhang, Y.; Shimoyama, I.; Wu, G. *J. Am. Chem. Soc.* **1989**, *111*, 8018. (d) Alabaster, R. J.; Cottrell, I. F.; Hands, D.; Humphrey, G. R.; Kennedy, D. J.; Wright, S. H. B. *Synthesis* **1989**, 598. (e) Lee, D.; Still, W. C. *J. Org. Chem.* **1989**, *54*, 4715. (f) Mills, R. J.; Taylor, N. J.; Snieckus, V. *Ibid.* **1989**, *54*, 4372. (g) Mills, R. J.; Snieckus, V. *Ibid.* **1989**, *54*, 4386. (h) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356. (i) Beak, P.; Snieckus, V. *Ibid.* **1982**, *15*, 306.

(3) Furukawa, N.; Shibutani, T.; Fujihara, H. *Tetrahedron Lett.* **1989**, *30*, 7091.

(4) (a) Anderson, K. K. *Tetrahedron Lett.* **1962**, 93. (b) Andersen, K. K.; Gaffield, W.; Papanikolaou, N. E.; Foley, J. W.; Perkins, R. I. *J. Am. Chem. Soc.* **1964**, *86*, 5637. (c) Herbrandson, H. F.; Dickerson, R. T., Jr.; Weinstein, J. *Ibid.* **1959**, *81*, 4102.

0022-3263/91/1956-5723$02.50/0