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A Convenient Synthesis of Alkali Metal Selenides and Diselenides in Tetrahydrofuran and the Reactivity Differences Exhibited by These Salts toward Organic Bromides. Effect of Ultrasound

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Introduction

Selenium and tellurium anions react with organic halides to form selenides, diselenides, tellurides, and ditellurides[1-5] (eq 1 and 2).

$$2RX + E_2^{2-} \rightarrow R_2E_2 \qquad (1)$$

$$2RX + E^{2-} \rightarrow R_2E \qquad (2)$$

R = alkyl, aryl; X = halogen; E = Se, Te

Historically, the syntheses of selenium salts of the type M_2Se_n (where M is an alkali metal and $n = 1$ or 2) were limited to liquid ammonia and protic solvents[4] (eq 3).

$$2M + nE \xrightarrow[110\ ^{\circ}C,\ 1\ h]{DMF} M_2E_n \qquad (3)$$

$$M = Na, K; E = Se, Te; n = 1, 2$$

Recently, however, Sandman and co-workers discovered that the species Na_2Se, Na_2Se_2, K_2Se, K_2Se_2, and their tellurium analogues could be produced by the direct reaction of selenium or tellurium powder with potassium or sodium in high-boiling, polar, aprotic solvents such as *N,N*-dimethylformamide (DMF), hexamethylphosphoramide (HMPA), or *N*-methylpyrrolidinone (NMP).[2]

Such direct alkali metal reductions of selenium and tellurium cannot be performed in the less polar solvent tetrahydrofuran (THF). Gladysz and co-workers found that lithium triethylborohydride will reduce elemental selenium in THF, producing Li_2Se or Li_2Se_2 depending on stoichiometry[5] (eq 4). This so-called "Super-Hydride" method is somewhat limited by scale and produces flammable byproducts.

$$nSe + 2Li(C_2H_5)_3BH \rightarrow Li_2Se_n + 2\ (C_2H_5)_3BH + H_2 \qquad (4)$$

$$n = 1, 2$$

Recently, Degrand and co-workers used a combination of electrochemical reduction and ultrasound to produce Se_2^{2-}, Se^{2-}, Te_2^{2-}, and Te^{2-}, in (THF), acetonitrile, and DMF.[3] These anions were trapped by benzyl chlorides and produced benzyl containing selenides, diselenides, tellurides, and ditellurides. With ultrasound, the electrochemical reduction of 1 mmol of selenium in acetonitrile in the presence of 2 mmol of benzyl chloride produced 0.5 mmol of benzyl selenide and trace amounts of benzyl diselenide.[3]

Table I. Reductions of Se by K, Na, and Li in THF[a]

reactn	reactn no.	conditions[b]	reductn time
I. $2K + 2Se \rightarrow K_2Se_2$	1	reflux	40 min
	2	ultrasound	85 min
	3	stir	150 min
II. $2K + Se \rightarrow K_2Se$	4	reflux	55 min
	5	ultrasound	120 min
	6	stir	300 min
IV. $2Na + 2Se \rightarrow Na_2Se_2$	7	reflux	65 min
	8	ultrasound	65 min
	9	stir	135 min
II. $2Na + Se \rightarrow Na_2Se$	10	reflux	80 min
	11	ultrasound	85 min
	12	stir	180 min
III. $2Li + 2Se \rightarrow Li_2Se_2$	13	reflux	8 h
	14	ultrasound	9.5 h
	15	stir	15 h
IV. $2Li + Se \rightarrow Li_2Se$	16	reflux	12 h

[a] Reductions performed in the presence of naphthalene (10 mol % with respect to the alkali metal). Reduction of Se to Na_2Se as performed with as little as 3 mol % naphthalene, requiring 7.5 h reflux for completion. Determination of reduction time is discussed in the Experimental Section. [b] All ultrasound and stirring reactions were performed at room temperature except for 8 and 9, which was performed at 35–40 °C.

Our interest in the effects of ultrasound on heterogeneous reactions[6] led us to examine the effects of ultrasound on the reaction of alkali metals with selenium powder in THF. We wish to report our results involving a procedure which allows for the convenient formation of any selenides and diselenides of lithium, sodium, or potassium in THF. We also wish to report on the effect of ultrasound on these reactions, as well as our results on the relative reactivities of Li_2Se_2, Li_2Se, and their sodium and potassium analogues in THF.[7]

Results and Discussion

We have found that the reduction of selenium by sodium or potassium does not occur after 24 h of reflux in THF. However, the addition of a small amount of naphthalene in the reaction mixture allows for the formation of not only the sodium and potassium selenides and diselenides but their lithium analogoues as well. Ultrasound at room temperature substantially accelerates the rates of these alkali metal naphthalide reductions of selenium over stirring at room temperature.

Table I indicates that in refluxing THF and in the presence of catalytic amounts of naphthalene, potassium will reduce selenium faster than sodium, which is in turn faster than lithium. However, for reductions of selenium at room temperature in THF, sodium is the best reducing agent, followed by potassium and lithium. Presumably a considerable amount of potassium will melt in refluxing THF, and this phase change may result in enhanced rates of selenium reduction. With room-temperature stirring, formation of K_2Se_2 is approximately as fast as Na_2Se_2, but

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(1) Reviews on selenium chemistry: (a) Klayman, D. L.; Gunther, W. H. H. *Organic Selenium Compounds*; *Their Chemistry and Biology*; Wiley: New York, 1973. (b) Clive, D. L. *Tetrahedron* **1982** *34*, 1049–1132. (c) Lotta, D. *Acc. Chem. Res.* **1984**, *17*, 28–34. (d) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22–30. (e) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 1.

(2) (a) Sandman, D. J.; Stark, J. C.; Acampora, L. A.; Gagne, P. *Organometallics* **1983**, *2*, 549–551. (b) Sandman, D. J.; Stark, J. C.; Foxman, B. M. *Organometallics* **1982**, *1*, 739–742.

(3) Gautheron, B.; Tainturier, G.; Degrand, C. *J. Am. Chem. Soc.* **1985**, *107*, 5579–5581.

(4) (a) Chugaev, L.; Choplin, W. *Ber.* **1914**, *47*, 1269–1275; *Chem. Abstr.* **1914**, *8*, 3400. (b) California Research Group. Br. Pat. 631 464, 1949. (c) Leicester, H. M., *Org. Synth.* 1943, *2*, 238–239. (d) Brandsma, L.; Wigers, H. *Recl. Trav. Chim. Pays-Bas* **1963**, 68. (e) Lalancette, J. M.; Arnac, M. *Can. J. Chem.* **1969**, *47*, 3695–3697. (f) Klayman, D. L.; Griffin, T. S. *J. Am. Chem. Soc.* **1973**, *95*, 197–199. (g) Bergman, J.; Engman, L. *Org. Prep. Prop. Proc. Int.* **1978**, *10*, 289. (h) Engman, L. *Organometallics* **1986**, *5*, 427–431.

(5) Gladysz, J, A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204–1208.

(6) For recent reviews on the effect of ultrasound on heterogeneous reactions: (a) Boudjouk, P. *J. Chem. Educ.* **1986**, *63*, 427–429. (b) Boudjouk, P. In *High Energy Processes in Organometallic Chemistry*; ACS Symposium Series No. 333; Suslick, K. S., Ed.; American Chemical Society: Washington, DC, 1987.

(7) Sodium selenide produced in this manner reacts with diorganosilanes to form cyclic silaselenanes, which are sources of dialkylsilaselones $R_2Si{=}Se$: Thompson, D. P.; Boudjouk, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1466–1467.

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Table II. Reactions of Selenides and Diselenides with Alkyl Bromides in THF

$$M_2Se_n + 2RX \rightarrow RSe_nR + 2MX$$

entry	Se salt	halide	conditions[a]	product	yield[c] %
1	Li_2Se	$C_6H_5CH_2Br$	0–5 °C, 1.5 h, stir	$(C_6H_5CH_2)_2Se$	80
2	Na_2Se	$C_6H_5CH_2Br$	0–5 °C, 1.5 h, stir	$(C_6H_5CH_2)_2Se$	85
4	Na_2Se	$C_6H_5CH_2Br$	0–5 °C, 45 min[b]	$(C_6H_5CH_2)_2Se$	85
5	Li_2Se_2	$C_6H_5CH_2Br$	0–5 °C, 5 min, stir	$(C_6H_5CH_2)_2Se$	>95
6	Na_2Se	$C_6H_5CH_2CH_2Br$	12 h, stir	$(C_6H_5CH_2CH_2)_2Se$	40
7	Na_2Se	$C_6H_5CH_2CH_2Br$	12 h[b]	$(C_6H_5CH_2CH_2)_2Se$	50
8	K_2Se	$C_6H_5CH_2CH_2Br$	2 h, reflux	$(C_6H_5CH_2CH_2)_2Se$	83
9	K_2Se	$C_6H_5CH_2CH_2Br$	4.5 h, reflux	$(C_6H_5CH_2CH_2)_2Se$	95
10	Na_2Se	$C_6H_5CH_2CH_2Br$	4.5 h, reflux	$(C_6H_5CH_2CH_2)_2Se$	80
11	Na_2Se	$C_6H_5CH_2CH_2Br$	6 h, reflux	$(C_6H_5CH_2CH_2)_2Se$	90
12	Na_2Se	$C_6H_5CH_2CH_2Br$	9 h, reflux	$(C_6H_5CH_2CH_2)_2Se$	>95
13	Li_2Se	$C_6H_5CH_2CH_2Br$	4.5 h, reflux	$(C_6H_5CH_2CH_2)_2Se$	25
14	Li_2Se	$C_6H_5CH_2CH_2Br$	9 h, reflux	$(C_6H_5CH_2CH_2)_2Se$	54
15	K_2Se_2	$C_6H_5CH_2CH_2Br$	4.5 h, stir	$(C_6H_5CH_2Ch_2)_2Se$	70
16	K_2Se_2	$C_6H_5CH_2CH_2Br$	13 h, stir	$(C_6H_5CH_2CH_2)_2Se$	95
17	Na_2Se_2	$C_6H_5CH_2CH_2Br$	45 min, stir	$(C_6H_5CH_2CH_2)_2Se$	81
18	Li_2Se_2	$C_6H_5CH_2CH_2Br$	5 min, stir	$(C_6H_5CH_2CH_2)_2Se_2$	>95
19	Na_2Se	2-octyl-Br	12 h, reflux	$(2\text{-octyl})_2Se$	0
20	Li_2Se	2-octyl-Br	12 h, reflux	$(2\text{-octyl})_2Se$	0
21	Na_2Se_2	2-octyl-Br	12 h, reflux	$(2\text{-octyl})_2Se_2$	>95
22	Na_2Se_2	2-octyl-Br	12 h[b]	$(2\text{-octyl})_2Se_2$	38
23	Na_2Se_2	2-octyl-Br	16 h[b]	$(2\text{-octyl})_2Se_2$	50
24	Li_2Se_2	2-octyl-Br	1 h[b]	$(2\text{-octyl})_2Se_2$	87
25	Li_2Se_2	2-octyl-Br	1 h, stir	$(2\text{-octyl})_2Se_2$	90

[a] Typically, approximately 1 g of selenium was reduced by the alkali metal in 25 mL of THF in the presence of naphthalene (10 mol % with respect to the alkali metal). The organic halide was added after reduction was complete. Unless otherwise specified, reactions were run at room temperature. [b] Reaction performed in an ultrasonic cleaning bath. [c] Yields determined by H^1 NMR.

formation of K_2Se is considerably slower than Na_2Se. This may indicate that under the conditions of the experiment, potassium reduction of K_2Se_2 to K_2Se is slower than sodium reduction of Na_2Se_2 to Na_2Se.

For lithium, sodium, and potassium reductions, if the reaction flask is partially submerged in a bath ultrasonic cleaner at a point generating maximum agitation in the flask, reduction is substantially enhanced over stirring at room temperature. In the case of sodium, ultrasonically induced reduction rates at room temperature rival reduction rates in refluxing THF. Presumably the mechanism responsible for this acceleration involves the ability of ultrasound to clean and pit the surfaces of the alkali metals,[8] which accelerates the formation of the alkali metal naphthalide.[9] For potassium, the rate of reduction of selenium in refluxing THF is considerably faster than for room-temperature ultrasound. This may also be attributable to a potassium phase change in refluxing THF which does not occur with room temperature ultrasound.

The in situ reduction of selenium by potassium, sodium, or lithium in THF produces suspensions of selenide or diselenide salts. The relative reactivities of these suspensions toward aliphatic bromides have been investigated. Although these results are qualitative, they demonstrate the considerable reactivity differences of these species in THF.

Diselenide salts exhibit a much greater activity than selenides toward organic halides in THF. Of the diselenide salts, Li_2Se_2 is more than an order of magnitude more reactive than Na_2Se_2 (Table II, entries 23 and 24). Interestingly, Na_2Se is apparently two to three times more reactive than Li_2Se (Table II, entries 10 vs 14). When (2-bromoethyl)benzene is added with stirring to Li_2Se_2 in THF, an immediate exothermic reaction ensues, which brings the solvent to near boiling. After 2 min the reaction begins to cool, and diselenide formation is complete within 5 min (Table II, entry 18). When (2-bromoethyl)benzene is added with stirring to Na_2Se_2 in THF, the reaction mixture warms slightly and begins to cool after approximately 40 min. Diselenide formation is not complete after 45 min (Table II, entry 17). The addition of (2-bromoethyl)benzene with stirring to Li_2Se or Na_2Se in THF produces no increase in the temperature of the reaction mixture. After 9 h of reflux, the Na_2Se reaction is complete, while the Li_2Se reaction produces only 54% yield (Table II, entries 12 and 14).

Lithium and sodium were found to be more convenient to work with than potassium, and studies involving potassium selenides and diselenides were somewhat limited. However, reactions of K_2Se and K_2Se_2 with the primary alkyl bromide (2-bromoethyl)benzene clearly show the trends found with its sodium and lithium analogues. Potassium diselenide is found to be the least reactive of the diselenide salts studied. The addition of (2-bromoethyl)benzene with stirring to K_2Se_2 in THF produces no change in temperature in the flask. After 4.5 h of stirring, the reaction is only 70% complete (Table II, entry 15). Potassium selenide is found to be the most reactive of the selenide salts studied. Reaction of K_2Se and (2-bromoethyl)benzene is 95% complete after 4.5 h (Table II, entry 9).

Ultrasound does little to accelerate the room temperature reactions of M_2Se and M_2Se_2 with organic halides in THF. If the reactions of alkali metal selenide and diselenide salts with aliphatic bromides in THF are homogeneous due to partial solubility of the alkali metal selenides, reaction rates may be unaffected by ultrasound. Ultrasound waves do not increase the rate of reaction of saturated solutions of Li_2Se_2 with 2-bromooctane over room-temperature stirring (Table II, entries 24 vs 25) and cause only a slight rate increase vs stirring in the reaction of Na_2Se with (2-bromoethyl)benzene in (Table II, entries 6 vs 7). However, at 0 °C, ultrasonic waves produce a twofold increase over stirring in the rate of reaction of

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[8] (a) Suslick, K. S.; Johnson, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 6856–6858. (b) Willard, C. W. *J. Acous. Soc. Am.* **1953**, *25*, 669–686. (c) Nappiras, E. A.; Noltingk, B. E. *Proc. Phys. Soc.* **1951**, *96*, 1032–1044.

[9] Ultrasound accelerates the reductions of cyclooctatetraene, anthracene, and acenaphthene to their dilithio dianionic salts: Boudjouk, P.; Sooriyakumaran, R.; Han, B.-H. *J. Org. Chem.* **1986**, *51*, 2818–2819.

benzyl bromide with Na_2Se (Table II, entries 2 and 5).

The formation of selenides and diselenides of lithium, sodium, and potassium can be accomplished in THF if a small amount of naphthalene is used as a soluble charge-transfer agent. This procedure allows for the convenient syntheses of these alkali metal selenides and diselenides and to our knowledge marks the first studies of Na_2Se, Na_2Se_2, K_2Se, and K_2Se_2 produced in situ in THF. The room temperature formation of selenide and diselenide salts may be substantially accelerated by simply placing the reaction flask into an ultrasonic bath. Relative rates of reduction based on the alkali metal are in the order K > Na > Li in refluxing THF and Na > K > Li at room temperature. Relative rate studies reported in Table II indicate both the extreme reactivity advantage diselenide salts exhibit over selenide salts in THF and that the reactivities of the selenide and diselenide salts are dependent on the counterion.

relative reactivities toward organic bromides in THF:

$$Li_2Se_2 \gg Na_2Se_2 \gg K_2Se_2 \gg K_2Se > Na_2Se > Li_2Se$$

We are continuing to study the reactions of these alkali metal selenides and diselenides with a variety of organic, organometallic, and inorganic halides.

Experimental Section

Tetrahydrofuran was distilled under nitrogen from sodium/benzophenone ketyl immediately before use. Selenium powder (Aldrich, 100 mesh) and all commercially available organic halides were used without further purification. Sodium pellets (3 to 8 mm) and lithium wire (3.2 mm diameter) were cut into chips before use. Potassium chips were cut from a potassium ingot.

Proton NMR spectra were obtained with a Varian EM-390 spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard 5880A GC with methyl silicone capillary column. All GC/MS analyses were performed on a Hewlett-Packard Model 5992 instrument. Melting points were obtained with a Thomas capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories.

Ultrasound experiments were conducted by partially submerging the reaction flask in a fan-cooled Bransonic Model 220 bath sonicator at a point generating maximum agitation in the flask. Ultrasound experiments at 0–5 °C were conducted by placing ice–water into the sonic bath. The temperature of the bath water was monitored with a thermometer, and the water was changed when its temperature rose above 5 °C.

Preparation of Metal Selenides and Diselenides. In a typical preparation, a clean, dry, three-neck, round-bottom flask equipped with condenser, magnetic stirrer, and nitrogen inlet was charged with selenium powder (0.72 g, 0.009 mol), THF (25 mL), sodium chips (0.42 g, 0.018 mol), and naphthalene (0.23 g, 0.0018 mol). The mixture was refluxed for approximately 1 h. During this time, the mixture changed from black to deep red to very light purple to white. Reductions performed in a slight excess of sodium would eventually turn a light green. After reflux, the white mixture was allowed to settle, leaving a white solid above a colorless liquid. The reaction mixture was then stripped of solvent. The white solid which remained was tested with water and indicated no residual sodium. Similar experiments were performed with diselenide salts, which were found to be reddish brown.

Similar experiments were performed to determine the reduction time of selenium by potassium to form K_2Se. A 2–1 mol mixture of potassium and selenium and a catalytic amount of naphthalene was stirred. The mixture would initially turn green and then dark brown after approximately 5 min. The mixture would then lighten considerably and eventually turn green for a second time after approximately 1 h. This green color would persist for another 4.5 h until reduction was complete, producing a metallic grey powder.

For individual syntheses of selenide and diselenide salts used for reaction with alkyl bromides, water tests could not be performed to ensure complete alkali metal consumption. These reductions were allowed to proceed for an extra period of time to ensure that no traces of alkali metal remained (it was observed that stirring selenide or diselenide suspensions for extended periods of time under nitrogen did not affect their reactivity).

Synthesis of Organoselenides and Diselenides. I. Synthesis of Dibenzyl Selenide. In a clean, dry, three-neck, round-bottom flask equipped with condenser magnetic stirrer, and nitrogen inlet were placed selenium powder (2.22 g, 0.028 mol) THF (25 mL), sodium chips (1.29 g, 0.056 mol), and naphthalene (0.72 g, 0.0056 mol). The mixture was refluxed for about 1 h, becoming white, and then refluxed for an extra 2 h to ensure completion of reduction. The reaction flask was cooled to 0 °C and benzyl bromide (6.6 mL, 9.5 g, 0.056 mol) added by syringe. The mixture was stirred at 0 °C for 5 min and at room temperature for 30 min. The mixture was filtered and the yellow filtrate stripped of solvent. The light orange oily residue was crystallized from hexane/ethanol to give light yellow crystals of benzyl selenide, mp 44–46 (lit. mp 45–46).[10] NMR ($CDCl_3$): δ 7.1 (s, C_6H_5), 3.8 (s, CH_2). Yield, 7.0 g or >95%. Relative rate data were obtained by comparing NMR integrated ratios of the methylene protons of benzyl bromide (δ 4.4) and the methylene protons of benzyl selenide.

II. Synthesis of Dibenzyl Diselenide. In a clean, dry, three-neck, round-bottom flask equipped with condenser, magnetic stirrer, and nitrogen inlet were placed selenium powder (1.5 g, 0.019 mol), THF (25 mL), lithium chips (0.26 g, 0.038 mol), and naphthalene (0.49 g, 0.0038 mol). The mixture was refluxed for 8 h, becoming a dark reddish brown. The mixture was refluxed for an extra 5 h to ensure complete consumption of the lithium and then cooled to 0 °C. Benzyl bromide (4.5 mL, 6.47 g, 0.038 mol) was added slowly by syringe. After being stirred for 5 min at 0 °C, the reddish brown slurry became an orange solution. The solution was stripped of THF and the residue added to benzene. The benzene mixture was then filtered and the filtrate stripped of solvent. The orange semisolid which remained was recrystallized from hexane/ethanol. The orange crystals recovered were identified as benzyl diselenide: mp 90–91 °C (lit. mp 91–92 °C);[11] NMR ($CDCl_3$) δ 7.1 (s, C_6H_5), 3.9 (s, CH_2). Subsequent runs were analyzed by comparison of the NMR integrated ratios of the methylene protons of the diselenide and the methylene protons of the starting material benzyl bromide.

III. Synthesis of Bis(2-phenylethyl) Selenide. In a clean, dry, three-neck, round-bottom flask equipped with condenser, magnetic stirrer, and nitrogen inlet were placed selenium powder (0.65 g, 0.008 mol), THF (25 mL), sodium chips (0.38 g, 0.016 mol), and naphthalene 0.21 g, 0.0016 mol). The mixture was stirred at room temperature for about 3 h, the black reaction mixture turning white. The reaction mixture was stirred for an extra 3 h to ensure complete consumption of the sodium. (2-Bromoethyl)benzene (2.25 mL, 3.05 g, 0.016 mol) was added slowly to the reaction flask by syringe, with stirring. The reaction mixture was stirred at room temperature for 30 min and then refluxed for 4 h. The mixture was allowed to cool to room temperature, the white solid settling to reveal a yellow liquid. An aliquot of the reaction mixture was analyzed by NMR, and indicated 82% conversion to product. The mixture was filtered, and the filtrate was stripped of solvent. The oily orange residue was chromatographed on silica gel, first with hexane and then benzene. A yellow band was eluted through the column with benzene. The benzene eluent was collected and stripped of solvent. The yellow liquid which remained was analyzed by NMR (CCl_4): δ 7.2 (s, C_6H_5), 2.7–3.0 (broadened q, CH_2CH_2). No signals attributable to starting material or naphthalene were observed. Analysis by GC/MS (hexane): m/z 289, ($(C_6H_5CH_2CH_2)_2Se$), 184 ($C_6H_5CH_2CH_2Se$), 105 ($C_6H_5CH_2CH_2$). Yield, 1.85 g or 78%. Subsequent runs of this reaction were analyzed by comparison of NMR integrated ratios of the methylene protons of the selenide and the methylene protons of the starting (2-bromoethyl)benzene.

IV. Synthesis of Bis(2-phenylethyl) Diselenide. In a clean, dry, three-neck, round-bottom flask equipped with condenser, magnetic stirrer, and nitrogen inlet were placed selenium powder (0.85 g, 0.011 mol), THF (25 mL), sodium chips (0.25 g, 0.011 mol),

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(10) Fromm, E.; Martin, K. *Ann.* **1913**, *401*, 177.

(11) Zincke, T.; Fries, K. *Annalen* **1904**, *334*, 342.

and naphthalene 0.14 g, 0.0011 g). The mixture was stirred for about 2 h, at which time no sodium was visible. The mixture was stirred for an extra 2 h to ensure complete consumption of the sodium. To the brownish colored reaction mixture, (2-bromoethyl)benzene (1.47 mL 0.011 mol) was added slowly by syringe at room temperature with stirring. The mixture warmed slightly after addition. After being stirred for 30 min at room temperature, the mixture changed color to a light orange. The mixture was stirred for an extra 30 min, and then an aliquot was removed, stripped of solvent, added to CCl$_4$, filtered, and analyzed by NMR spectroscopy. Integration of the methylene protons of the starting halide and methylene protons of the product indicated 80% conversion. The reaction mixture was filtered and the filtrate stripped of solvent. The oily, orange residue was chromatographed on silica gel, first with hexane and then with benzene. An orange band was eluted with benzene and stripped of solvent. The orange liquid which remained was analyzed by NMR (CCl$_4$): δ 7.2 (s, C$_6$H$_5$), 3.2–3.0 (broadened t, CH$_2$CH$_2$); no signals attributable to starting material or naphthalene were observed. Analysis by GC/MS (in hexane): 368 ((C$_6$H$_5$CH$_2$CH$_2$)$_2$Se$_2$), 291 (loss of C$_6$H$_5$), 263 (C$_6$H$_5$CH$_2$CH$_2$Se), 115 (C$_6$H$_5$CH$_2$CH$_2$). Yield, 2.97 g or 75%. Subsequent reactions were analyzed by comparison of NMR integrated ratios of methylene protons of diselenide and methylene protons of the starting (2-bromoethyl)benzene.

V. Synthesis of Di-2-octyl Diselenide. In a clean, dry, three-neck, round-bottom flask equipped with condenser and nitrogen inlet were placed selenium powder (1.25 g, 0.016 mol), THF (25 mL), lithium wire (0.11 g, 0.016 mol), and naphthalene (0.20 g, 0.0016 mol). The reaction flask was partially submerged in a fan-cooled bath sonicator and sonicated. After 9 h, no lithium was visible in the flask. The flask was sonicated for an extra 5 h to ensure complete consumption of the lithium. Into the flask was syringed 2-bromooctane (2.5 mL, approximately 0.016 mol) without interruption of sonication. Within 1 h after halide addition, the reaction mixture turned from brown to orange. An aliquot of the solution was removed, and observed to have undergone 87% conversion by NMR integration. The orange solution was stripped of solvent and the oily orange residue dissolved in hexane. The hexane solution was filtered and stripped of solvent. The orange oil which remained was chromatographed on silica gel with hexane. A greenish band was eluted through the column in 5-mL increments. Analysis of the second aliquot by capillary GC indicated only naphthalene (comparison with authentic standard) and product. The aliquot was sublimed at room temperature to remove naphthalene, leaving a greenish liquid. Anal. Calcd for C$_{16}$H$_{34}$Se$_2$: C, 49.98; H, 8.93. Found: C, 49.66; H, 8.73. NMR (C$_6$D$_6$): δ 2.7–3.2 (m, SeCH). Subsequent runs were analyzed by NMR comparison of SeCH with BrCH of starting 2-octylbromide as well as comparison of SeCH vs all aliphatic protons.

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Regioselective Palladium-Catalyzed Arylation of Vinyl Ethers with 4-Nitrophenyl Triflate. Control by Addition of Halide Ions

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For effective use of enol ethers in palladium-mediated vinylic substitution reactions,[1] procedures for selective substitution at either the α-[2] or β-olefinic[3] carbon are desirable.

Table I. Reaction of 4-Nitrophenyl Triflate with Butyl Vinyl Ether in DMF in the Presence of Lithium Halides (LiX)[a]

LiX added	β/α	cis/trans	yield, %[b]
none	1.5	0.5	82
LiCl	13	0.6	68
LiBr	14	0.9	74
LiI	5.2	1.4	23

[a] The triflate (5 mmol), butyl vinyl ether (10 mmol), triethylamine (6 mmol), lithium halide (10 mmol), and palladium acetate (0.05 mmol) were heated at 95 °C in 12 mL of DMF for 18 h. [b] GLC yields; not optimized. 4,4'-Dinitrobiphenyl and minor amounts of 4-nitrophenol and bis(4-nitrophenyl) ether accounted for remaining material.

In a recent report we presented results from a systematic study of factors governing the regiochemistry of arylation reactions of enol ethers with halobenzenes.[4] It was established that the halide exerts a considerable influence on regiochemistry. In that study, 4-nitrobromobenzene and 4-nitroiodobenzene were important reagents since (i) assessment of the influence of halide on regioselectivity, both in the presence and absence of phosphine ligand, was possible,[5] and (ii) formation of stable products allowed accurate determination of isomeric distributions.[6]

Aryl triflates[7] and, particularly, vinyl triflates[8] have been proven to serve as useful precursors to organopalladium intermediates. Stille and co-workers reported that aryl[7a] or vinyl[9] triflates undergo palladium-catalyzed coupling reactions with organotin reagents, provided lithium chloride is present in the medium. It was proposed that a vinylpalladium chloride complex is the species which undergoes transmetalation with the organotin reagent.

This finding suggested that various arylpalladium halide intermediates would be accessible from aryl triflates and the appropriate halide salts. Hence, we decided to examine the potential of this approach with respect to regiocontrolled Heck arylation of electron-rich olefins.

Here, we report that the presence of lithium or tetrabutylammonium halides strongly affects the regiochemical outcome as well as the reaction rate in palladium-catalyzed reactions of 4-nitrophenyl triflate with butylvinyl ether.

Results and Discussion

The arylation reactions were performed at 95–100 °C under standard Heck arylation conditions, using 1% palladium acetate as catalyst precursor and triethylamine as base. The results obtained from addition of lithium

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(1) For recent reviews, see: (a) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic: London, 1985. (b) Heck, R. F. *Org. React. (N.Y.)* 1982, *27*, 345–390.

(2) (a) Lee, T. D.; Daves, G. D., Jr. *J. Org. Chem.* 1983, *48*, 399. (b) Hallberg, A.; Westfelt, L.; Holm, B. *Ibid.* 1981, *46*, 5414. (c) Arai, I.; Daves, G. D., Jr. *Ibid.* 1979, *44*, 21. (d) Arai, I.; Daves, G. D., Jr. *Ibid.* 1978, *43*, 4110.

(3) (a) Hallberg, A.; Westfelt, L.; Andersson, C.-M. *Synth. Commun.* 1985, *15*, 1131. (b) Andersson, C.-M.; Hallberg, A. *J. Org. Chem.* 1988, *53*, 235.

(4) Andersson, C.-M.; Hallberg, A.; Daves, G. D., Jr. *J. Org. Chem.* 1987, *52*, 3529.

(5) Reactions employing nonactivated bromobenzenes normally require a phosphine ligated palladium catalyst; see ref 1.

(6) We have observed extensive product decomposition under the conditions in reactions starting from electron-rich halobenzenes.

(7) (a) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* 1987, *109*, 5478. (b) Cacchi, S.; Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* 1986, 3931. (c) Chen, Q.-Y.; Yang, Z.-Y. *Ibid.* 1986, 1171. (d) Cacchi, S.; Ciattini, P. G.; Morera, E.; Ortar, G. *Ibid.* 1986, 5541.

(8) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 508–524. (b) Scott, W. J.; Pena, M. R.; Swärd, K.; Stoessel, S. J.; Stille, J. K. *J. Org. Chem.* 1985, *50*, 2302. (c) Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* 1984, 2271.

(9) (a) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* 1986, *108*, 3033. (b) Crisp, G. T.; Scott, W. J.; Stille, J. K. *Ibid.* 1984, *106*, 7500. (c) Scott, W. J.; Crisp, G. T.; Stille, J. K. *Ibid.* 1984, *106*, 4630.

0022-3263/88/1953-2112$01.50/0