$J_{10,11}$ = 3.0 Hz), 7.00 (s, 1, H_9), 7.87–8.43 (m, 8, Ar).

(+)-(9*R*,10*S*)-9,10-Epoxy-9,10,11,12-tetrahydrobenzo[*e*]pyrene ((+)-BePE). A solution of (−)-**1b** (54 mg, 0.1 mmol) and NaOMe (16 mg) in methanol (3 mL) and THF (3 mL) was stirred at room temperature under N_2 for 2.5 h. The product was partitioned between ether and water, and the ether layer was dried and evaporated. Trituration of the residue with cold ether–hexane (1:1) afforded (+)-BePE (20 mg, 74%) as a white solid: mp 132–133 °C; $[\alpha]^{23}_D$ +332.2° (0.475 g/100 mL, $CHCl_3$); NMR (500 MHz) δ 2.02 (m, 1, H_{11}), 2.70 (m, 1, H_{11}), 3.00 (m, 1, H_{12}), 3.58 (dd, 1, H_{12}), 3.93 (s, 1, H_{10}), 4.90 (d, 1, H_9, $J_{9,10}$ = 4.4 Hz), 7.98–8.05 (m, 4, $H_{2,4,5,7}$), 8.16 (d, 2, $H_{3,6}$, $J_{2,3}$ = $J_{6,7}$ = 7.5 Hz), 8.35 (d, 1, H_1, $J_{1,2}$ = 8.0 Hz), 8.61 (d, 1, H_8, $J_{7,8}$ = 8.0 Hz).

(−)-(9*S*,10*R*)-9,10-Epoxy-9,10,11,12-tetrahydrobenzo[*e*]pyrene ((−)-BePE). Analogous reaction of (+)-**1b** furnished (−)-BePE: $[\alpha]^{23}_D$ −330.2° (0.525 g/100 mL, $CHCl_3$); the NMR spectrum of (−)-BePE was superimposable on that of (+)-BePE.

(+)-(9*S*,10*S*)-*trans*-10-Bromo-9-hydroxy-9,10,11,12-tetrahydrobenzo[*e*]pyrene ((+)-1a). A mixture of (+)-**1b** (84 mg, 0.15 mmol) and $LiAlH_4$ (6 mg) in anhydrous ether (10 mL) was stirred at room temperature for 30 min under anhydrous conditions. The reaction mixture was decomposed by addition of dilute acetic acid, and the ether phase was washed with water, dried, and evaporated to yield an oil. Crystallization from EtOAc gave (+)-**1a** (53 mg, 99%) as a white solid: $[\alpha]^{23}_D$ +10.6° (0.625 g/100 mL, THF); the NMR spectrum of (+)-**1a** was identical with that of the racemic **1a**.

(−)-(9*R*,10*R*)-*trans*-10-Bromo-9-hydroxy-9,10,11,12-tetrahydrobenzo[*e*]pyrene ((−)-1a). Analogous reaction of (−)-**1b** furnished (−)-**1a**: $[\alpha]^{23}_D$ −10.0° (0.54 g/100 mL, THF); the NMR spectrum of (−)-**1a** matched that of the racemic **1a**.

***trans*-10-Bromo-9-(*p*-methoxybenzoyloxy)-9,10,11,12-tetrahydrobenzo[*e*]pyrene (1c).** A solution of (+)-**1a** (10 mg, 0.028 mmol) and excess *p*-methoxybenzoyl chloride in pyridine (0.2 ml) was left at room temperature overnight. After the usual workup, trituration of the solid residue with cold ether gave 12.6 mg of white solid. Preparative TLC of the ether phase on silica gel eluted with benzene gave another 1 mg of product, affording a total of 13.6 mg (99%) of **1c**: mp 166–167 °C; NMR δ 2.6 (m, 2, H_{11}), 3.7 (m, 2, H_{12}), 3.8 (s, 3, OCH_3), 5.0 (m, 1, H_{10}), 6.8–7.3 (m, 4, Ar), 7.8–8.6 (m, 9, Ar). The CD spectrum of this diastereomer of **1c** (Figure 1) exhibited a negative first Cotton effect at 277 nm and a positive second Cotton effect at 254 nm, allowing assignment of its configuration as 9*S*,10*S*.

Similar treatment of (−)-**1a** gave the other enantiomer of **1c** the CD spectrum of which was a mirror image of the first, confirming its absolute configuration as 9*R*,10*R*.

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Registry No. (±)-**1a**, 88767-14-0; (+)-(9*S*,10*S*)-**1a**, 88824-51-5; (−)-(9*R*,10*R*)-**1a**, 88824-52-6; (+)-(9*S*,10*S*)-**1b**, 88824-53-7; (−)-(9*R*,10*R*)-**1b**, 88767-15-1; (9*S*,10*S*)-**1c**, 88780-81-8; (9*R*,10*R*)-**1c**, 88851-60-9; (+)-(9*R*,10*S*)-BePE, 88824-54-8; (−)-(9*S*,10*R*)-BePE, 88824-55-9; 9,10-dihydrobenzo[*e*]pyrene, 66788-01-0; (−)-menthoxyacetyl chloride, 15356-62-4; *p*-methoxybenzoyl chloride, 100-07-2.

Notes

Synthesis of Tetrathiafulvalene Doubly Fused to the 3,4-Position of Selenophene

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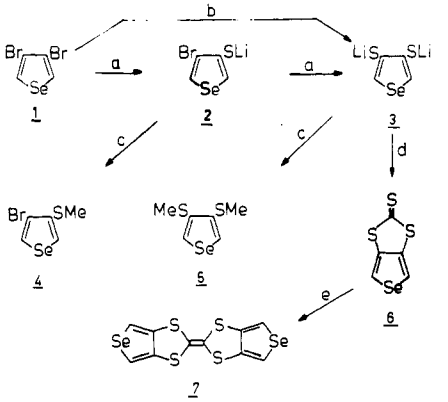
Tetrathiafulvalenes have received much attention in recent years as electron donors for preparation of electrical-conducting charge-transfer complexes.[1] Annelation of aromatic rings on the thiafulvalene system[2] and the use of selenium[3] and tellurium[4] analogues have provided interesting structural modifications. The goal of this work was to prepare the tetrathiafulvalene fused on both rings to the 3,4-position of selenophene.

Scheme I



(a) 1 BuLi; S_8 · (b) 2 BuLi; S_8 ·

(c) excess CH_3I · (d) $CSCl_2$ · (e) $P(OMe)_3$

Since the most general method for preparation of such tetrathiafulvalenes involves coupling of an appropriately substituted thione[5] or selenone,[6] our first synthetic goal

(1) (a) Narita, M.; Pittman, C. U., Jr. Synthesis **1976**, 489. (b) Engler, E. M.; Patel, V. V.; Andersen, J. R.; Schumaker, R. R.; Fukushima, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 3769. (c) Cowan, D. O.; Kini, A.; Chiang, L.-Y.; Lerstrup, K.; Talham, D. R.; Poehler, T. O.; Bloch, A. N. *Mol. Cryst. Liq. Cryst.* **1982**, *86*, 1741/1.

(2) (a) Nakayama, J. *Synthesis* **1975**, 168. (b) Lerstrup, K.; Lee, M.; Wiygul, F. M.; Kistenmacher, T.; Cowan, D. O. *J. Chem. Soc., Chem. Commun.* **1983**, 294. (c) Johannsen, I.; Bechgaard, K.; Mortensen, K.; Jacobsen, C. *Ibid.* **1983**, 295.

(3) (a) Chiang, L.-Y.; Cowan, D. O.; Poehler, T. O.; Bloch, A. N. *Mol. Cryst. Liq. Cryst.* **1982**, *86*, 1767/27. (b) Bechgaard, K.; Cowan, D. O.; Bloch, A. N. *J. Chem. Soc., Chem. Commun.* **1974**, 937. (c) Fanghänel, E.; Schukat, G.; Schützenübel, J. *Z. Chem.* **1981**, *21*, 447. (d) Engler, E. M.; Green, D. C. *J. Chem. Soc., Chem. Commun.* **1976**, 148.

(4) Wudl, F.; Aharon-Shalom, E. *J. Am. Chem. Soc.* **1982**, *104*, 1154.

(5) Miles, M. G.; Wager, J. S.; Wilson, J. D.; Siedle, A. R. *J. Org. Chem.* **1975**, *40*, 2577. (b) Hünig, S.; Kiesslich, G.; Quast, H.; Scheutzow, D. *Liebigs Ann. Chem.* **1973**, 310. (c) Scherowsky, G.; Weiland, J. *Chem. Ber.* **1974**, *107*, 3155. (d) Le Coustumer, G.; Mollier, Y. *J. Chem. Soc., Chem. Commun.* **1980**, 38.

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was the 1,3-dithiolo[4,5-*c*]selenophene-2-thione from 3,4-dibromoselenophene by the procedure outlined in Scheme I. Initial attempts using two alternate halogen–metal exchanges and thiolations with butyllithium and elemental sulfur to give the dilithium salt of the dithiol followed by reaction with carbon disulfide[7] failed to provide any of the desired product.

In order to monitor the progress of the reaction at various stages the intermediate mono- and dithiol lithium salts were trapped by addition of methyl iodide. Thus, reaction of the dibromide with 1 equiv each of butyllithium and sulfur followed by excess methyl iodide provided a good yield of the bromo methylthio compound **4**. Characterization of the product mixture by GC, MS, and NMR showed that it was 80% **4** in addition to unreacted dibromide, bromoselenophene, and (methylthio)selenophene as well as a small amount of the bis(methylthio)-selenophene (**5**). Similarly, treatment with methyl iodide after two reaction cycles with butyllithium and sulfur provided a good yield of bis(methylthio)selenophene (**5**), which crystallized after distillation. GC and MS analyses of the product mixture showed some mono- and dibromoselenophenes, bromo(methylthio)selenophene, and (methylthio)selenophene. Thus it was clear that the reactions had proceeded as expected up to the point of the dilithiothioselenophene. Formation of a small amount of the bis(methylthio)selenophene after only one reaction sequence with butyllithium and sulfur indicated that some of the dilithioselenophene was formed and that it reacted further with sulfur and methyl iodide to give **5**. The reaction of **1** with 2 equiv of butyllithium followed by 2 equiv of sulfur and an excess of methyl iodide gave the same product (**5**) albeit in smaller amount and lower purity. The dilithioselenophene appears to be less stable to possible ring-opening reactions,[8] which leads to polymers. Thus two alternate halogen–metal exchange–sulfurization sequences[9] were established as being the better route to the dilithiothio intermediate **3**.

Several attempted ring-closure reactions with carbon disulfide failed to provide the bicyclic product. It was postulated that this failure resulted from the fact that after the first reaction with carbon disulfide the actual ring-closure step must involve attack of the negative thiolate on the negatively charged trithiocarbonate. This should predispose the system to alternate polymerization or ring-opening reactions. Although a variety of thiocarbonic acid derivatives might have been chosen, we attempted first the reaction with thiophosgene, which gave an overall yield of 17% **6** from dibromoselenophene **1**. This is actually a five-step sequence and the average yield per step is 70%.

Several procedures are available for conversion of dithiolanethiones to tetrathiafulvalenes,[6,7] but the simplest, when it is successful, is the use of a trivalent phosphorus compound.[10] In fact trimethyl phosphite provides a 54% yield of **7**.

The thiophene analogue of **7** can also be prepared in 32% yield by coupling thieno[3,4-*d*]-1,3-dithiol-2-thione with trimethyl phosphite. The convenience of this procedure plus the slight improvement in yield makes this the method of choice in comparison with the previously reported[9] four-step synthesis from the same precursor.

Experimental Section

Melting points were determined on a Leitz hot stage and are uncorrected. NMR spectra were measured on a JEOL HM 100 spectrometer in $CDCl_3$, unless noted otherwise; chemical shifts are reported in δ values downfield relative to tetramethylsilane as an internal standard. GC analyses were performed on a Perkin-Elmer Model 900 chromatograph using a 2-m column of 10% BDS on Chromosorb W programmed from 70 to 200 °C. MS were determined on a Finnigan Model 4021 spectrometer, using an ionizing voltage of 70 eV, except as noted. Elemental analyses were performed at the Analytical Department at the Lund University Chemical Center or at the Ilse Beetz Microanalytical Laboratory, Kronach, West Germany.

3,4-Dibromoselenophene (1) was prepared from selenophene by tetrabromination in acetic acid followed by selective debromination with 2 equiv of butyllithium.[11]

3-Bromo-4-(methylthio)selenophene (4). 3,4-Dibromoselenophene (**1**, 5.8 g, 0.02 mol) was dissolved in 20–25 mL of absolute ether and cooled to −78 °C. Butyllithium (14 mL of 1.47 M, 0.02 mol) in hexane was added dropwise to the stirred solution under a nitrogen atmosphere. After being stirred for an additional 5 min, sulfur (0.65 g, 0.02 mol) was added and the reaction mixture was stirred for 5 min. Methyl iodide (2 mL, 0.03 mol) in 10 mL of ether was added dropwise with stirring, and the mixture was allowed to warm to room temperature. Ice, water, and more ether were added to the reaction mixture and the ether phase was separated, dried, and concentrated in a rotatory evaporator. The dark oil was distilled (80–90 °C (0.6 mmHg)) to give 2.0 g of product. According to GC this material is about 80% **4**, 5% each of **1** and 3-bromoselenophene, and smaller amounts of 3-(methylthio)selenophene and **5**. Each fraction was characterized by GC and MS. MS of **4**: M^+ observed m/e (relative intensity) 252, (5), 253 (5), 254 (17), 255 (5), 256 (34), 258 (27), 260 (5) (calcd relative intensity, 4.5, 4.0, 16.5, 4.0, 37.0, 29.5, 4.5, respectively). ^1H NMR: δ 2.42 (3 H, CH_3), 7.40 (1 H, d, J = 3.0 Hz, 5-H), 7.91 (1 H, d, J = 3.0 Hz, 2-H), J_{Se} = 57 Hz.

3,4-Bis(methylthio)selenophene (5). Method A. To 3,4-dibromoselenophene (**1**, 5.8 g, 0.02 mol) in 10 mL of ether at −78 °C was added butyllithium (14 mL, 1.47 M, 0.02 mol) in hexane dropwise with stirring and under nitrogen. The reaction mixture was stirred for another 5 min, and sulfur (0.65 g, 0.02 mol) was added and the mixture was stirred for 15 min. The addition of butyllithium and sulfur was repeated, and the mixture was stirred for 30 min. Methyl iodide (8.0 g, 0.06 mol) was added and the mixture was allowed to warm to room temperature. Ice was added to the reaction mixture, which was then extracted three times with ether, and the organic phases were combined, dried, and evaporated. The dark oil was distilled (100–110 °C (0.6 mmHg)) in a short-path distillation apparatus to give 2.8 g of product shown by GC analysis to be about 80% **6** together with small amounts of starting material, 3-bromoselenophene, **4**, and 3-(methylthio)selenophene. The product partly solidified on refrigeration and after recrystallization from petroleum ether (40–60 °C) melted at 57–58 °C: MS, m/e (relative intensity) M^+ observed 220 (8), 221 (10), 222 (24), 224 (45), 226 (11) (calcd relative intensity, 9, 7.5, 24, 50, 9, respectively); ^1H NMR δ 2.45 (6 H, s, CH_3), 7.60 (2 H, s, H-2,5), J_{Se} = 45 Hz. Anal. Calcd for $C_6H_8S_2Se$: C, 32.28; H, 3.62. Found: C, 32.15; H, 3.58.

Method B. The above procedure was modified by dropwise addition of 0.04 mol of butyllithium followed by addition of 0.04 equiv of sulfur. Quenching with methyl iodide and workup as above gave 2 g of distillate, which by GC was about 60% **6**, with larger amounts of the other products found in procedure A. This material also partly solidified on refrigeration.

1,3-Dithiolo[4,5-*c*]selenophene-2-thione (6). The bis(thiolithio) salt **3** was prepared as described above for method A. After the second addition of sulfur, thiophosgene (2 mL) in 10 mL of ether was added dropwise at −78 °C. The reaction mixture was stirred for an additional 30–40 min and then allowed to warm

(6) Engler, E. M.; Patel, V. V. *Tetrahedron Lett.* **1976**, 423.
(7) (a) Gronowitz, S.; Moses, P. *Acta Chem. Scand.* **1962**, *16*, 205. (b) Gronowitz, S.; Moses, P.; Hörnfeldt, A.-B. *Arkiv Kemi* **1961**, *17*, 237.
(8) (a) Gronowitz, S.; Frejd, T. *Khim. Geterotsikl. Soedin* **1978**, 353.
(9) Shu, P.; Chiang, L.; Emge, T.; Holt, D.; Kistenmacher, T.; Lee, M.; Stokes, J.; Poehler, T.; Bloch, A.; Cowan, D. *J. Chem. Soc., Chem. Commun.* **1981**, 920.
(10) Pittman, C. U.; Jr.; Narita, M.; Liang, Y. F. *J. Org. Chem.* **1976**, *41*, 2855.
(11) Dell'Erba, C.; Spinelli, D.; Garbarino, G.; Leandri, G. *J. Heterocycl. Chem.* **1968**, *5*, 45.

to room temperature, whereupon it was poured into ice with stirring and then ether was added. The ether, water, and solid phases were separated, and the water phase was extracted with ether. The solid was washed repeatedly with ether, and the ether phases were combined, dried, and concentrated. The dark residue was sublimed to give yellow crystals. These were washed with petroleum ether and recrystallized from chloroform–hexane to give 0.68 g of product with a melting point of 156–161 °C. Chromatography (chloroform–hexane) of the residue from the combined mother liquor and the petroleum ether washes followed by sublimation and recrystallization gave an additional 0.11 g: mp 155–161 °C; total yield 0.79 g (17%). Further recrystallization from chloroform–hexane gave a product melting from 160–161.5 °C: MS, *m/e* (relative intensity) M^+ 234 (9), 235 (8), 236 (22), 238 (46), 240 (15) (calcd relative intensity, 9, 7.5, 24, 50, 9, respectively); ^1H NMR δ 7.84 (4). Anal. Calcd for $C_5H_2S_3Se$: C, 25.32; H, 0.85. Found: C, 25.25; H, 0.87.

$\Delta^{2,2'}$-Bis(1,3-dithiolo[4,5-*c*]selenophene) (7). The thione 6 (0.60 g, 2.5 mmol) was heated under reflux in trimethyl phosphite (9 mL) in a nitrogen atmosphere. The reactant dissolved and a precipitate formed in 15 min. The reaction was continued for 1.75 h and then refrigerated. The product was collected by filtration and washed with ether, 0.25 g of 1 was obtained, and the melting point was 260–263 °C. Chromatography of the filtrate (silica gel, ethyl acetate) gave 30 mg of product, mp 256–262 °C, total yield 0.28 g (54%): MS (ionizing potential = 19 eV), *m/e* (relative intensity) M^+ 406 (6.2), 407 (4.8), 408 (15.3), 409 (10), 410 (26.0), 412 (base peak, 29.0), 414 (11.5) (calcd relative intensity, 4.7, 3.6, 14.8, 7.5, 25.6, 29.3, 9.0, respectively); ^1H NMR (Me_2SO-d_6) δ 7.97 (s). Anal. Calcd for $C_{10}H_4S_4Se_2$: C, 29.27; H, 0.99. Found: C, 29.65; H, 0.77.

$\Delta^{2,2'}$-Bithieno[3,4-*d*]-1,3-dithiole. Thieno[3,4-*d*]-1,3-dithiol-2-thione[7] (0.19 g, 1 mmol) was heated under reflux in a nitrogen atmosphere in 1.2 mL of trimethyl phosphite for 2 h, during which time a small amount of crystals had formed. After refrigeration, 0.05 g (32%) of crystals were obtained, mp 260–263 °C (lit.[9] mp 259–260 °C). Chromatography of the mother liquor gave a small amount of the product: MS, *m/e* 316 (M^+, base peak), 158 (M^{2+}).

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Registry No. 1, 17422-59-2; 3, 88609-68-1; 4, 82451-15-8; 5, 88589-46-2; 6, 88589-47-3; 7, 88609-67-0; $\Delta^{2,2'}$-bithieno[3,4-*d*]-1,3-dithiole, 80229-45-4; thieno[3,4-*d*]-1,3-dithiol-2-thione, 80229-39-6; selenophene, 288-05-1; 3-bromoselenophene, 25109-24-4; 3-(methylthio)selenophene, 35577-04-9.

Dicyclohexylphosphide as an Auxiliary Ligand for Thermally Stable Heterocuprates with Considerably Improved Reactivity. Some Beneficent Effects of LiBr on Cuprate Reactivity

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Organocuprates, RR'CuLi, have been the most useful class of organometallic reagents for C–C bond formation developed during the past 2 decades and one of the most useful ever developed.[1] In spite of their importance, systematic comparisons of organocuprate stability and reactivity have not been undertaken until recently.[2] Such studies of thermal stability[3] have resulted in the development of new heterocuprates (R' = PPh_2, NCy_2) that have the highest stability and still maintain high reactivity.[4] However, in some reactions these new cuprates were still too far away from our goal of a high yield with but 1.0 equiv of R. This is essential if cuprate reactions are to be used to make the key C–C bonds in convergent syntheses.[5] We have now found that the use of dicyclohexylphosphide (PCy_2) as the auxiliary ligand gives thermally stable cuprates with considerably improved reactivity. In the course of these studies, we observed that the presence of LiBr has a beneficent effect on the yields of product.

Results and Discussion

Organocuprates are generally prepared by adding an organolithium reagent to a Cu(I) halide such as CuI or $CuBr{\cdot}SMe_2$;[6] consequently, they contain 1 equiv of halide from the metathesis reaction (eq 1). Unless special steps

$$CuBr + RLi \rightarrow RCu + LiBr \quad (1)$$

$$RCu + R'Li \rightarrow RR'CuLi \quad (2)$$

are taken, the product of eq 2 contains the equivalent of LiBr from eq 1, whether the second lithium reagent added is RLi (homocuprate) or $LiPR_2$ (heterocuprate). Organic chemists generally ignore the fact that this LiBr is present.

For R = Me the preparation of halide-free cuprates is especially easy, since MeCu is extremely insoluble in ether or THF, allowing the ether-soluble Li halide to be extracted from it.[7] On the other hand, Me_2CuLi with extra equivalents of halide present can be obtained by using MeLi·LiBr or adding LiBr. The same expedients can be used to prepare the corresponding heterocuprates[8] containing various amounts of halide. The results of our studies, which utilized substrates representing four of the most important classes of synthetically useful cuprate reactions,[9] are summarized in Table I. Before detailing these results we emphasize that 1.0 equiv of $RCu(PCy_2)Li$ was used, rather than the 2–5-fold excesses of R_2CuLi commonly used.[10–12]

(1) Posner, G. H. "An Introduction to Synthesis Using Organocopper Reagents"; Wiley: New York, 1980.

(2) For leading references to recent studies, see: (a) Lipshutz; B. H.; Parker, D.; Kozlowski, J. A.; Miller, R. D. *J. Org. Chem.* **1983**, *48*, 3334. (b) Johnson, C. R.; Dhanoa, D. S. *J. Chem. Soc., Chem. Commun.* **1982**, 358. (c) Tsuda, T.; Yazawa, T.; Watanabe, K.; Fujii, T.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 192.

(3) Bertz, S. H.; Dabbagh, G. *J. Chem. Soc., Chem. Commun.* **1982**, 1030.

(4) Bertz, S. H.; Dabbagh, G.; Villacorta, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 5824.

(5) For example, in a number of convergent prostaglandin syntheses, the optically active (and therefore valuable) side chain is attached by using a homocuprate (R_2CuLi) to make the C(12)–C(13) bond; see ref 1, p 41, 43, 97.

(6) We have found this precursor to give superior results for both homocuprates and heterocuprates. In fact our phosphido cuprates cannot be prepared from CuI due to reduction to Cu.

(7) Casey, C. P.; Cesa, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4236. We used this procedure for halide-free MeCu with the following modifications: $CuBr{\cdot}SMe_2$ was used at 0 °C rather than $CuI(SBu_2)_2$ at −78 °C. When the MeCu thus obtained was hydrolyzed with H_2O, no LiBr was detected by $AgNO_3$ titration.

(8) For the reactions in Table I, the heterocuprates were prepared by using Method B of ref 4. See the Experimental Section.

(9) That our heterocuprates give high yields with an acid chloride is demonstrated by our thermal stability studies (ref 3 and 4). Allylic halides are more reactive than the alkyl halide we used here and would not have provided as challenging a test.

(10) Whitesides, G. M.; Fischer, W. F.; San Filippo, J.; Bashe, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871. Inspection of the data in Table IV of this paper reveals the same trend with increasing LiI that we observe with increasing LiBr.

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