Chromium tricarbonyl complexed haloarenes were prepared following known procedures[16,17] and had been already described.[15,18]

General Procedure. $Cr(CO)_3$-complexed haloarenes (2,15 mmol) and thiols (2,37 mmol) were dissolved in benzene (25 mL) and stirred under nitrogen with a 10–50% NaOH solution (25 mL) or with solid ground NaOH (6.45 mmol) in the presence of a phase-transfer catalyst, whose molar ratio with respect to the substrate was 0.28 for TOAB, 0.37 for CTAB, and 0.56 (apparent:hygroscopic) for aliquat 336. The reaction progress was monitored by TLC (silica gel; eluant: Et_2O/light petroleum, 1/2). At the end of the reaction the organic layer was washed with water and dried over Na_2SO_4, and the solvent was removed at reduced pressure. The product was usually characterized after decomplexation by treatment of the crude chromium compound with iodine in Et_2O at 0 °C. The nature of the phase-transfer catalyst used in each reaction, reaction conditions, and yields of isolated products are summarized in Table I.

Uncomplexed Alkyl Aryl Sulfides. Compounds **2** were identified by comparison with authentic samples prepared according to literature procedures.

Tricarbonyl(isopropyl phenyl sulfide)chromium: mp 50 °C; IR ($CHCl_3$) 1970, 1890 cm^{-1} ($\nu_{C=O}$); ^1H NMR δ 1.35 (d, 6 H), 3.25 (m, 1 H), 5.25 (m, 5 H).

Anal. Calcd for $C_{12}H_{12}CrO_3S$: C, 49.99; H, 4.20. Found: C, 49.90; H, 4.40.

Tricarbonyl(*tert*-butyl phenyl sulfide)chromium: mp 93 °C; IR ($CHCl_3$) 2000, 1925 cm^{-1} ($\nu_{C=O}$); ^1H NMR δ 1.30 (s, 9 H), 5.25 (m, 3 H), 5.50 (m, 2 H).

Anal. Calcd for $C_{13}H_{14}CrO_3S$: C, 51.64; H, 4.69. Found: C, 51.48; H, 4.84.

Acknowledgment. We acknowledge financial support by CNR Progetto Finalizzato Chimica Fine e Secondaria.

Registry No. 1 (Ar = Ph, R = *i*-Pr), 84029-36-7; 1 (Ar = Ph, R = *t*-Bu), 72068-09-8; $Cr(CO)_3PhF$, 12082-05-2; $Cr(CO)_3PhCl$, 12082-03-0; $Cr(CO)_3$-*m*-MePhCl, 33411-11-9; $Cr(CO)_3$-*p*-MePhCl, 12116-24-4; MeS^-, 17302-63-5; *n*-BuS^-, 20733-16-8; *i*-PrS^-, 20733-15-7; *t*-BuS^-, 20733-19-1; TOAB, 14866-33-2; CTAB, 57-09-0.

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Generation and Ring Opening of 2,3-Dilithio-1-(phenylsulfonyl)indole

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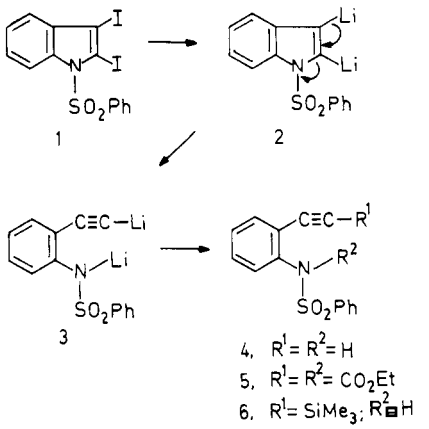
We recently reported[1] the generation of 3-lithio-1-(phenylsulfonyl)indole, a species which is stable at −100 °C but which cleanly rearranges to the more stable 2-lithio-1-(phenylsulfonyl)indole upon warming to room temperature, and we also discussed the possibility that this indole lithiation methodology could provide a synthetic equivalency for 2,3-dilithio-1-(phenylsulfonyl)indole (**2**). We now describe the apparent transient generation of **2** and its subsequent facile ring opening to lithium 2-(*N*-lithiophenylsulfonamido)phenylacetylide (**3**) at −100 °C.

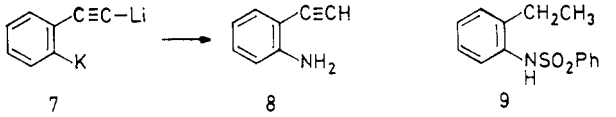
Treatment of 2,3-diiodo-1-(phenylsulfonyl)indole (**1**, which can be prepared from indole in 86% yield[1]) with 4 equiv[2] of *tert*-butyllithium [tetrahydrofuran (THF), −100 °C] results in the immediate formation of a yellow-orange color. After 3–5 min at −100 °C this solution is treated with various electrophiles (ammonium chloride, ethyl chloroformate, trimethylsilyl chloride) to give the products **4–6** in 66–82% yield (Scheme I).

Scheme I



Although we had hoped that the indole ring would retain its integrity in this reaction, it was clear from the IR and ^1H and ^{13}C NMR spectra of the products **4–6** that an acetylenic functionality was present. Thus, the IR spectrum of **4** shows a strong acetylenic C–H stretching absorption at 3315 cm^{-1}, and the IR spectra of **5** and **6** show C≡C absorption at 2210–2150 cm^{-1}.[3] The ^1H NMR spectrum of **4** displays the acetylenic proton at 3.38 ppm,[4] and the ^{13}C NMR spectra of **4–6** exhibit the expected[5] range of chemical shifts (78.4–102.2 ppm) for the acetylenic carbons.

Final structural proof was established both by an independent synthesis of **4** and by conversion of **4** to a known compound. Thus, the known[6] dimetalated phenylacetylide **7** is aminated with methoxylamine to give (2-amino-



phenyl)acetylene (**8**) in low yield. A Hinsberg reaction[7] on **8** gives a compound that is identical with **4** as obtained from **1**. In addition, catalytic hydrogenation of **4** gives the known[8] ethyl derivative **9**, which is identical with a sample prepared from 2-ethylaniline by a Hinsberg reaction. Thus, the structure of **4** is firmly secured as [2-(phenylsulfonamido)phenyl]acetylene.

We believe that this exceedingly rapid ring-opening reaction (observed even at −120 °C) involves the intermediacy of **2**, rather than cleavage of a monolithiated intermediate followed by the second halogen–metal interchange to give **3**. The aversion of both 2- and 3-lithio-1-(phenylsulfonyl)indole to undergo comparable ring-opening reactions,[1] even at higher temperatures, argues strongly against a stepwise process for the formation of **3**.

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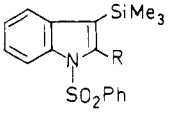
Direct evidence for the intermediacy of **2** lies in the fact that we also isolate 1-(phenylsulfonyl)indole (18% yield) and a 2:1 mixture (not separated) of 2,3-bis(trimethylsilyl)-1-(phenylsulfonyl)indole (**10**) and 3-(trimethylsilyl)-1-(phenylsulfonyl)indole (**11**) (13% yield) after quenching the reaction mixture with ammonium chloride and trimethylsilyl chloride, respectively. These minor products are presumably formed by the reaction of **2** and the electrophile before the former can ring open to **3**. The formation of **11** in the reaction with trimethylsilyl chloride indicates, not unexpectedly, that the 3-position in **2** is the more reactive site. The resulting monolithiated species **12** is sluggish[9] to further reaction with the second equivalent of trimethylsilyl chloride and, upon workup, affords **11** in addition to **10**.



10, R = $SiMe_3$
11, R = H
12, R = Li

When **1** is treated with 1 equiv of *tert*-butyllithium (−100 °C) and quenched with ammonium chloride, a mixture of **1**, **4**, and 2- and 3-iodo-1-(phenylsulfonyl)indole is obtained (^{13}C NMR), indicating little or no regioselectivity in the halogen–metal exchange reaction.

Although there are several examples of heterocyclic ring-opening reactions involving monolithiated intermediates in furan,[10] benzofuran,[11] thiophene,[12] benzothiophene,[13] isothiazole,[14] and related heterocyclic[14,15] chemistry, only a few examples of anionic ring-cleavage processes involving 1,2-dilithio heterocycles are known. Thus, 3,4-diiodofuran,[16] 2,5-diphenyl-3,4-diiodothiophene,[17] and 2,3-dibromobenzo[*b*]selenophene[18] all undergo bis halogen–metal exchange with *n*-butyllithium, and the resulting latter two dilithio species undergo ring opening similar to that observed herein. All of these ring-opening reactions occur at higher temperatures than that of the **2** → **3** conversion, which may be facilitated by the generation of two highly stabilized anions (phenylacetylide and phenylsulfonanilide[19]).

Experimental Section

Melting points were determined with a Mel-Temp Laboratory Devices apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. Infrared spectra were recorded on a Perkin-Elmer 599 instrument. ^1H NMR spectra were obtained with a Hitachi Perkin-Elmer R-24 spectrometer, and ^{13}C NMR spectra were measured on a JEOL FX60Q Fourier transform NMR spectrometer. Tetramethylsilane was the internal reference. "Flash chromatography" refers to the technique developed by Still,[20] and the grade of silica used was 230–400 mesh. Thin-layer chromatography was performed on precoated (0.2 mm) silica gel 60 F_{254} plastic sheets (E. Merck). The *tert*-butyllithium was standardized by titration against 2,5-dimethoxybenzyl alcohol.[21] Tetrahydrofuran was distilled from sodium/benzophenone ketyl. All reactions were performed in oven-dried (130 °C) glassware under prepurified argon.

General Lithiation Procedure. A magnetically stirred solution of 2,3-diiodo-1-(phenylsulfonyl)indole[1] (**1**) in dry THF under argon was cooled to −100 °C. This solution was treated rapidly via syringe with 4 equiv of *tert*-butyllithium (2.1 M in pentane) and stirred at −100 °C for 3–5 min. The resulting yellow-orange mixture was immediately quenched in situ with various electrophiles (vide infra) and stirred at approximately −100 °C for 30 min. The mixture was warmed slowly to room temperature, poured into 5% aqueous $NaHCO_3$ (125 mL), and extracted with CH_2Cl_2 (4 × 60 mL). The combined extracts were washed with H_2O (1 × 100 mL) and brine (2 × 100 mL), dried (K_2CO_3), and evaporated in vacuo to afford the crude product which was purified as described below.

2-(Phenylsulfonamido)phenylacetylene (4). The crude product obtained from the lithiation of **1** (2.55 mmol) in dry THF (65 mL) and quenching with 5% aqueous NH_4Cl (8 mL) was flash chromatographed over silica gel. Sequential elution with 1:1 and 2:1 Et_2O–hexane gave initially 0.12 g (18%) of 1-(phenylsulfonyl)indole followed by 0.53 g (81%) of **4** as a light amber oil after drying at 40 °C (0.2 torr). This material crystallized after 4 days at 5 °C: mp 65–66 °C; IR ($CHCl_3$) 3350 (s), 3315 (s), 1495 (s), 1455 (s), 1405 (s), 1348 (s), 1174 (s), 917 (s), 597 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 8.13–6.80 (m, 10 H), 3.38 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 138.8, 138.1, 133.0, 132.3, 130.0, 128.8, 127.1, 124.2, 119.5, 112.8, 84.2, 78.4. Anal. Calcd for $C_{14}H_{11}NO_2S$: C, 65.35; H, 4.31; N, 5.44; S, 12.46. Found: C, 65.33; H, 4.32; N, 5.44; S, 12.42.

The same result was obtained at −120 °C using a THF/Et_2O/hexane/pentane (8:2:2:1) solvent system.

Ethyl 2-(*N*-Carbethoxyphenylsulfonamido)phenylpropiolate (5). The crude product obtained from the lithiation of **1** (1.01 mmol) in dry THF (40 mL) and quenching with freshly distilled ethyl chloroformate (2.30 mmol) was flash chromatographed over silica gel. Elution with CH_2Cl_2 gave an amber viscous oil which immediately crystallized on drying at 0.4 torr to provide 0.269 g (66%) of analytically pure **5** as a colorless solid: mp 93–94 °C; IR (KBr) 2210 (s), 1742 (s), 1704 (s), 1448 (s), 1354 (s), 1298 (s), 1266 (s), 1195 (s), 1172 (s), 852 (s), 750 (d), 720 (d), 595 (s), 571 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 8.23–7.92 (m, 2 H), 7.77–7.20 (m, 7 H), 4.13 (q, 4 H, J = 7.5 Hz), 1.25 (t, 3 H, J = 7.5 Hz), 1.14 (t, 3 H, J = 7.5 H); ^{13}C NMR ($CDCl_3$) δ 152.8, 151.2, 138.7, 138.3, 134.0, 133.6, 131.4, 131.2, 129.3, 129.2, 128.4, 120.2, 84.7, 81.3, 63.8, 61.8, 13.9. Anal. Calcd for $C_{20}H_{19}NO_6S$: C, 59.84; H, 4.77; N, 3.49; S, 7.99. Found: C, 59.61; H, 5.03; N, 3.44; S, 7.93.

[2-(Phenylsulfonamido)phenyl]trimethylsilylacetylene (6). The crude product obtained from the lithiation of **1** (0.524 mmol) in dry THF (23 mL) and quenching with freshly distilled chlorotrimethylsilane (2.20 mmol) was flash chromatographed over silica gel. Elution with 3:1 cyclohexane–CH_2Cl_2 gave an oil which crystallized on drying at 0.5 torr to afford 0.142 g (82%) of analytically pure **6** as colorless crystals: mp 82–83 °C; IR (KBr) 3275 (s), 2150 (s), 1495 (s), 1405 (s), 1345 (s), 1248 (s), 1174 (m), 920 (s), 845 (m), 755 (m), 688 (s), 545 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.95–6.87 (m, 10 H), 0.25 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 138.9, 137.9, 132.9, 131.9, 129.7, 128.8, 127.1, 124.3, 119.8, 114.3, 102.2, 99.3, −0.2. Anal. Calcd for $C_{17}H_{19}NO_2SSi$: C, 61.97; H, 5.81; N, 4.25; S, 9.73. Found: C, 62.27; H, 5.86; N, 4.12; S, 9.37.

A less polar material was also isolated from the flash column and found to be an inseparable mixture of **10** and **11** (ca. 2:1 by NMR integration) as a colorless oil, 26.5 mg (ca. 13%); partial ^1H NMR ($CDCl_3$) for **10** δ 0.23 (s, 9 H), 0.45 (s, 9 H); for **11** δ 0.30 (s, 9 H); mass spectrum, for **10** m/e (relative intensity) 401 (M^+, 25), 386 (75); for **11** m/e (relative intensity) 329 (M^+, 45), 314 (37).

Independent Synthesis of 4. Phenylacetylene (20.5 mmol) was converted to **7** according to the Brandsma procedure[6] and quenched at −50 °C with methoxylamine (22.6 mmol; prepared from the commercially available hydrochloride salt by the method of Gilman)[22] neat via syringe. The mixture was allowed to warm

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slowly to room temperature overnight, poured into Et_2O (200 mL), and extracted with 25% aqueous HCl (2 × 200 mL). The combined acidic aqueous portions were washed with Et_2O (1 × 125 mL) and then slowly neutralized with KOH pellets, while maintaining efficient cooling and stirring. The resulting basic (pH 10) aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL), and the combined extracts were washed with H_2O (1 × 150 mL) and brine (2 × 150 mL), dried (Na_2SO_4), and concentrated in vacuo to give crude (2-aminophenyl)acetylene (8) as a tan oil. Flash chromatography over silica gel with 6:4 hexane–Et_2O gave 0.110 g (5%) of pure 8 as a colorless viscous oil whose spectral properties matched the literature values:[3,4] IR (neat) 3480 (s), 3385 (s), 3295 (s), 2100 (s), 1612 (s), 1489 (s), 1450 (s), 1311 (s), 1255 (s), 1154 (s), 743 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.40–6.45 (m, 4 H), 4.50–3.85 (br s, 2 H), 3.32 (s, 1 H).

This sample of 8 (60 mg, 0.51 mmol) was treated with benzenesulfonyl chloride (0.53 g, 3.00 mmol) in 10% aqueous NaOH (8 mL). The mixture was stirred at room temperature for 2 h, warmed to 40 °C for 20 min, and diluted with H_2O (75 mL). The mixture was acidified with 20% aqueous HCl and extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were washed with 20% HCl (3 × 50 mL), 5% aqueous $NaHCO_3$ (1 × 50 mL), H_2O (1 × 50 mL), and brine (2 × 75 mL), dried (Na_2SO_4), and evaporated in vacuo in afford 73 mg (56%) of 4 as a light tan oil. Chromatography over silica gel with CH_2Cl_2 elution gave pure 4 which was identical in all respects (IR, TLC, UV, ^1H NMR, ^{13}C NMR) with material obtained via the lithiation/ring-opening route.

2-(Phenylsulfonamido)-1-ethylbenzene (9). A solution of pure 4 (obtained via the lithiation route; 118 mg, 0.459 mmol) in absolute ethanol (40 mL) was hydrogenated over 5% Pd/C (10 mg) in a 100-mL Parr apparatus at 3 atm of H_2 for 19 h. The catalyst was removed by filtration through a bed of Celite and thoroughly washed with ethanol. Concentration in vacuo gave a viscous oil which was purified by flash chromatography over silica gel with CH_2Cl_2 elution to afford 115 mg (96%) of pure 9 as a white solid after further drying at 0.2 torr: mp 110–111 °C (lit.[8] mp 101–102 °C); IR (KBr) 3250 (s), 2975 (s), 1453 (s), 1412 (s), 1332 (s), 1158 (s), 908 (s), 753 (s), 730 (s), 666 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.95–6.90 (m, 9 H), 6.84 (br s, 1 H), 2.41 (q, 2 H, J = 7.5 Hz), 1.03 (t, 3 H, J = 7.5 Hz).

This sample of 9 was identical (mixture melting point of 109–111 °C; IR, TLC, ^1H NMR) with material prepared by treating 2-ethylaniline with benzenesulfonyl chloride under the conditions described above.

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Registry No. 1, 80360-26-5; 2, 84416-63-7; 4, 84416-64-8; 5, 84416-65-9; 6, 84416-66-0; 8, 52670-38-9; 9, 84416-67-1; 10, 84416-68-2; 11, 80360-17-4; phenylacetylene, 536-74-3; benzenesulfonyl chloride, 98-09-9; 2-ethylaniline, 578-54-1.

One-Pot and Regioselective Synthesis of Alkenes and Deuterioalkenes from α-Chloro Carboxylic Acid Chlorides via a Tandem Addition of Two Different Nucleophiles (Grignard Reagents, Hydride or Deuteride) and Further Lithiation

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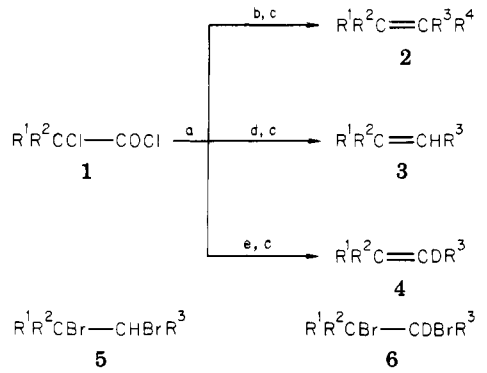
In previous papers we reported a new and regioselective "one-pot" method to obtain olefins and polyolefins from α-chloro carbonyl compounds, Grignard reagents or lithium aluminum hydride, and lithium powder.[1] The use of lithium aluminum deuteride instead of lithium aluminum hydride yields deuterioolefins.[1d] On the other hand, it was recently reported[2] that a convenient method to transform carboxylic acid chlorides into ketones is the reaction of an excess of carboxylic acid chloride with Grignard reagents in tetrahydrofuran at −78 °C. This last observation led us to study the stepwise addition of two different Grignard reagents, or one Grignard reagent and a hydride or deuteride, to α-chloro carboxylic acid chlorides with further lithiation to obtain olefins and deuterioolefins.

Scheme I[a]



[a] (a) R^3MgBr, THF, −78 to −60 °C; (b) R^4MgBr, Et_2O, −60 °C; (c) Li, −60 to 20 °C; (d) $LiAlH_4/AlCl_3$, Et_2O, −60 °C; (e) $LiAlD_4/AlCl_3$, Et_2O, −60 °C.

When an α-chloro carboxylic acid chloride (1) reacts with a Grignard reagent (1:1 molar ratio) in tetrahydrofuran between −78 and −60 °C and then a second Grignard reagent is added in ether at −60 °C, followed by reaction with lithium powder at −60 °C with slow heating to room temperature, the corresponding "mixed" olefin 2 was obtained (see Scheme I and Table I). If isomeric compounds Z/E are possible for compounds 2, a mixture of both isomers is obtained (GLC and NMR; table, entries 4–14). When very reactive Grignard reagents were used in the first step of the reaction, as allylic (R^3 = allyl) or benzylic (R^3 = $PhCH_2$) derivatives, results were not as good as for other alkylic derivatives. So, reaction with allylmagnesium bromide led in all cases to compounds resulting from the initial diaddition of the Grignard compound to the α-chloro carboxylic acid chloride, and the expected tandem addition did not take place. With benzylmagnesium bromide, yields were poor (table, entry 9), and toluene (20%) and dibenzyl (11%) were obtained as secondary products. When α-chloro carboxylic acid esters were the starting reagents, the two olefins from the stepwise double addition of R^3MgBr and R^4MgBr (2, R^3 = R^4) were obtained. The use of organocadmium compounds (made in situ from R^3MgBr and cadmium dichloride) for the initial step of the reaction rendered lower yields for olefin 2; for instance, 2b was

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