was heated at 70 °C for 1 h. After filtration through a filter paper to remove the excess of Raney nickel, the filtrate was eluted through a silica gel column (*n*-hexane/EtOAc, 1:1) and concentrated under reduced pressure. The products **8** and **9** were separated by HPLC (LiChrosorb, *n*-hexane/EtOAc, 2:1). Compounds **8** and **9** can be obtained alternatively by treating **5** (0.26 mmol), *n*-Bu_3SnH (1.04 mmol), and AIBN (0.034 mmol) in dry benzene (8 mL) at reflux overnight. The resulting solution was concentrated under reduced pressure, eluted through a silica gel column, and separated by HPLC to obtain the desulfurized products **8** and **9**.

3-Ethyl-3-sulfolene (8a): solid; mp 60–61 °C; IR (KBr) 1295 and 1250 (SO_2), 1110, 778 cm^{-1}; ^1H NMR δ 1.06 (t, J = 8 Hz, 3 H, CH_3CH_2), 2.16 (m, 2 H, CH_3CH_2), 3.65, 3.77 (2 s, 4 H, SO_2CH_2), 5.67 (s, 1 H, vinyl proton on the ring). This compound is now commercially available. The ^1H NMR spectrum is identical with that reported in the *Aldrich Library of NMR Spectra*, 2nd ed., Vol. 2, 786c.

3-Ethylidenesulfolane (9a): oil; IR (neat) 2955, 1642, 1405, 1310 and 1130 (SO_2), 882 cm^{-1}; ^1H NMR δ 1.62 (d, J = 8 Hz, 3 H, CH_3CH=C), 2.81–3.4 (m, 4 H, $SO_2CH_2CH_2$), 3.66 (s, 2 H, SO_2CH_2C), 5.6 (q, J = 8 Hz, 1 H, vinyl proton); MS m/z 146 (M^+), 81, 67 (100), 54, 53, 41. Anal. Calcd for $C_6H_{10}O_2S$: C, 49.3; H, 6.9. Found: C, 49.4; H, 6.8.

3-Propyl-3-sulfolene (8b): solid; mp 88–89 °C; IR (KBr) 2961, 1649, 1294 and 1117 (SO_2), 923, 814, 781 cm^{-1}; ^1H NMR δ 0.89 (t, J = 6.4 Hz, 3 H, CH_3CH_2), 1.44 (m, 2 H, CH_3CH_2), 2.14 (t, J = 7.2 Hz, 2 H, $CH_3CH_2CH_2$), 3.66, 3.75 (2 s, 4 H, 2 SO_2CH_2), 5.68 (s, 1 H, vinyl proton on the ring); MS m/z 160 (M^+), 131, 96, 81, 68 (100), 67, 41. Anal. Calcd for $C_7H_{12}O_2S$: C, 52.47; H, 7.55. Found: C, 52.49; H, 7.60.

3-Propylidenesulfolane (9b): oil; IR (neat) 2963, 1640, 1458, 1400, 1312 and 1128 (SO_2), 911, 885; ^1H NMR δ 0.95 (t, J = 7.2 Hz, 3 H, CH_3CH_2), 1.98 (m, 2 H, CH_3CH_2), 2.8–3.24 (m, 4 H, $SO_2CH_2CH_2$), 3.66 (s, 2 H, SO_2CH_2C), 5.58 (m, 1 H, vinyl proton); MS m/z 160 (M^+), 95, 81, 68, 67, 55, 54, 53, 41. Anal. Calcd for $C_7H_{12}O_2S$: C, 52.47; H, 7.55. Found: C, 52.31; H, 7.74.

3-(4-Methyl-4-pentenyl)-3-sulfolene (8c): oil; IR (neat) 1648 (C=C), 1237, 1317 and 1122 (SO_2), 891 cm^{-1}; ^1H NMR δ 1.60 [m, 2 H, $CH_3C(=CH_2)CH_2CH_2$], 1.69 [s, 3 H, $CH_3C(=CH_2)CH_2$], 2.12 [m, 4 H, $CH_3C(=CH_2)CH_2CH_2CH_2C$], 3.66, 3.76 (2 s, 4 H, 2 SO_2CH_2), 4.72 (s, 2 H, C=CH_2), 5.68 (s, 1 H, vinyl proton on the ring); MS m/z 136 (M - 64), 135, 107, 93, 81, 79, 69, 68, 67, 55, 53, 41 (100). Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.97; H, 8.05. Found: C, 59.86; H, 8.01.

3-(4-Methyl-4-pentenylidene)sulfolane (9c): oil; IR (neat) 2968, 1647, 1311 and 1129 (SO_2), 901, 818, 773 cm^{-1}; ^1H NMR δ 1.7 [s, 3 H, $CH_3C(=CH_2)CH_2$], 2.11 [br s, 4 H, $CH_3C(=CH_2)CH_2CH_2$], 2.75–3.3 (m, 4 H, $SO_2CH_2CH_2$), 3.67 (s, 2 H, SO_2CH_2C), 4.71 (br s, 2 H, C=CH_2), 5.61 (br s, 1 H, C=$CHCH_2$); MS (m/z 200 (M^+), 199, 145, 136, 135, 134, 133, 131, 121, 119, 117, 108, 107, 105, 93, 91, 81, 79, 77, 55 (100), 41. Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.97; H, 8.05. Found: C, 59.73; H, 8.14.

Synthesis of α-Myrcene (10). Thermolysis of **8c** to give α-myrcene was carried out by injecting **8c** on a preparative GC (injection temperature 240 °C, oven temperature 100 °C) with a SE-30 (3-m) column. The chromatogram showed the existence of only a single product, **10**, which was collected with a dry-ice trap. The ^1H NMR and IR spectra of **10** are identical with those in the literature.[10]

Acknowledgment. We thank the National Science Council of the Republic of China for financial support (Grant NSC78-0208-M001-18).

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Palladium-Catalyzed Reactions in the Synthesis of 3- and 4-Substituted Indoles. 4

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4-Bromo-1-tosylindole (**1**) was converted to tricyclic indole enone **11**, a potential intermediate in the synthesis of tetracyclic ergot alkaloids, by a series of palladium-catalyzed processes. Attempts to construct the ergot D ring by the hetero-Diels–Alder reaction of enone **11** and 1-azabutadiene **12** produced not the expected [4 + 2] adduct **13** but the benz[*cd*]indoline derivative **14** resulting from attack of the aza diene at the indole 2-position. The thermodynamic stability of the naphthol nucleus makes enone **11** generally susceptible to attack at the indole 2-position, as evidenced by the attack of hydride and methyl cuprate nucleophiles at this position forming indolines **16** and **17**, respectively.

Introduction

A general approach to the synthesis of 3,4-disubstituted indoles involving palladium(II)-catalyzed formation of 4-bromoindole and sequential introduction of carbon side chains at the 3- and 4-positions using palladium(0) catalysis has recently been developed in these laboratories[1] and has been applied to the synthesis of (±)-clavicipitic acid methyl ester[2] and (±)-aurantioclavine.[3] Herein is presented the use of related methodology to append the C ring of the tetracyclic ergot alkaloids,[4] as well as the results of attempts to annulate the D ring by aza diene cycloaddition chemistry[5] (eq 1).

Results and Discussion

4-Bromo-1-tosylindole, **1**, prepared by the palladium(II)-catalyzed cyclization of *N*-tosyl-2-ethenyl-3-bromoaniline,[1] is a versatile starting material for ergot alkaloid

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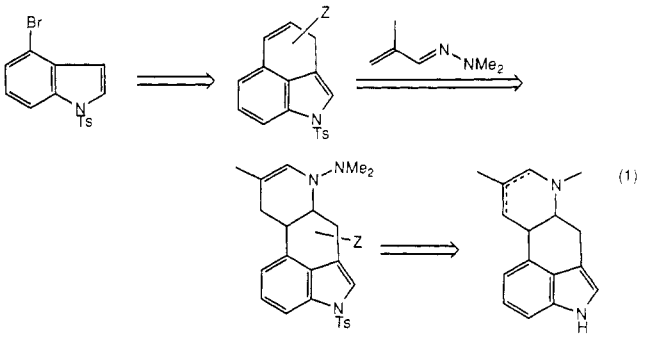
0022-3263/89/1954-4141$01.50/0



syntheses, since functionalization at the requisite 3- and 4-positions is readily accomplished by a variety of different transition metal assisted processes. Scheme I summarizes the approaches studied. The first approach involved introduction of the C-ring side chain at the 4-position followed by palladation of the electrophilic 3-position, olefin insertion, and β-hydride elimination. π-Allylnickel halide complexes are generally reactive toward aryl halides, replacing the halide with the allyl group under very mild conditions.[6] Treatment of bromoindole **1** with (2-carbethoxyallyl)nickel bromide in DMF produced unsaturated ester **2** in excellent yield. As is typical for π-allylnickel halide reactions, the side-chain olefin did not rearrange into conjugation. Direct palladation of indoles at the 3-position to give arylpalladium(II) intermediates which undergo both olefin and carbon monoxide insertion is known.[7] However, treatment of **2** with a variety of electrophilic palladium(II) species resulted in consumption of starting material but no cyclization to produce the desired tricyclic compound. Mercuration of indoles at the 3-position is also known[8] and occurred with **2** as well. However, the insoluble mercurio salt proved difficult to dry, and treatment with Li_2PdCl_4 regenerated **2** rather than resulting in transmetalation/insertion.

Since the olefinic side chain was unstable to the conditions and reagents required to functionalize at the 3-position of the indole, the sequence of steps was reversed. Direct mercuration of **1** produced 3-mercurioindole **3** in essentially quantitative yield. Treatment of this compound with allylic halides and a catalytic (1 mol %) amount of lithium chloropalladate, in a process involving transmetalation from mercury to palladium, olefin insertion into the arylpalladium(II) complex, and *β-halide* elimination (regenerating the palladium(II) halide catalyst)[9] produced 3-substituted indoles **4** and **5** in excellent yield. These compounds are perfectly set up for an intramolecular "Heck arylation", and indeed cyclization in the presence of catalytic amounts of palladium(0) occurred to form the desired C ring in good to excellent yield. Unfortunately, concomitant isomerization of the tricyclic indole to the thermodynamically more stable benz[*cd*]indoline ring system occurred[10] producing compounds **6** and **7**, which are unsuitable substrates for subsequent annulation of the D ring.

Treatment of mercurioindole **3** with acryloyl chloride and a catalytic amount of palladium(0) produced indole **8** in fair yield, in a process involving oxidative addition of the acid chloride to palladium(0), mercury–palladium(II) exchange, and reductive elimination to form **8** and reform the palladium(0) catalyst.[11] Indole **8** underwent facile palladium(0)-catalyzed cyclization to produce tricyclic ketone **11** in excellent yield. The keto group not only prevented rearrangement to the benz[*cd*]indoline system, it provided an appropriately activated α,β-unsaturated enone system for the planned D-ring annulation by an aza diene cycloaddition. [An alternative approach to indole **8** was less successful. Iodination of **3** led to 3-iodo-4-bromoindole **9** in excellent yield. Introduction of the acryloyl side chain[12] as an allenic ether using palladium(0)-catalyzed oxidative addition of the aryl iodide followed by transmetalation from zinc to palladium and reductive elimination formed **10** in reasonable yield. However, attempts to hydrolyze the allenic ether to the α,β-unsaturated enone were not successful.]

The *N,N*-dimethylhydrazone of methacrolein has proved to be a useful aza diene in cycloaddition reactions to conjugated enones and quinones.[5,13] The process is highly regioselective, with the 4-carbon of the aza diene adding to the β-position of the enone, and the nitrogen adding to the α-position. Addition in this sense to tricyclic ketone **11** would produce the correct tetracyclic ergot alkaloid ring system in a single step. Accordingly **11** was treated with 1-(dimethylamino)-3-methyl-1-azabuta-1,3-diene, and indeed, a one to one addition product was obtained in good yield. However, the product of this reaction was *not* the expected 4 + 2 cycloadduct **13**, but rather the unusual 1,4-addition product **14** (Scheme II), whose proposed structure is consistent with all of the physical data. The elemental analysis confirmed the empirical formula, $C_{24}H_{25}N_3SO_3$, and the mass spectrum had a parent ion at m/e 435 corresponding to this composition. A major fragment, m/e 323, corresponded to loss of the entire aza diene fragment (m/e 112, which was also an intense peak in the mass spectrum), indicating the likelihood for a single point of attachment for the aza diene fragment. The infrared spectrum had a strong OH band, no carbonyl band (**11** has a strong ν_{CO} at 1735 cm^{-1}) and strong bands at ν 1609 and 1561 cm^{-1}. (The aza diene has strong bands at ν 1617 and 1562 cm^{-1}.) The presence of a phenolic system was supported by the UV/visible spectrum, which had absorptions at λ_{max} 232, 285, and 342 nm (MeOH) which shifted to λ_{max} 244, 292, and 368 nm upon addition of base. (α-Naphthol showed a similar base-induced shift, from λ_{max} 230, 292 nm to λ_{max} 245, 330 nm.) The ^1H and ^{13}C NMR spectra further support the proposed structure. H_a (s, 7.18 δ), H_b (br s, 5.41 δ), and H_c (br s, 5.61 δ) correspond to those protons in the starting aza diene. The H_d, H_e, H_f system appeared as a typical ABX system: δ_d 3.13, δ_e 3.30, δ_f 5.55; J_{de} = 15.3 Hz, J_{df} = 2.7 Hz, J_{ef} = 5.2 Hz. The phenolic OH appeared as a singlet at 8.83 δ. Similarly C_1 (δ 139.4, d), C_3 (δ 122.4, t), C_4 (δ 39.6, t), and C_5 (δ 66.7, d) are consistent with the assigned structure. Treatment of indoline **14** with Raney nickel cleaved the N–N bond and reduced the aza diene system.[14] Reaction with ethyl formate produced formamide **15**. Spectroscopic evidence was again consistent with a tricyclic benz[*cd*]indoline nucleus.

The unusual course of the reaction between enone **11** and aza diene **12** is likely the result of the enhanced stability of the benz[*cd*]indoline system over the indole system (~20 kcal/mol).[10] Indeed, enone **11** was generally reactive toward nucleophilic addition to the 2-position, as

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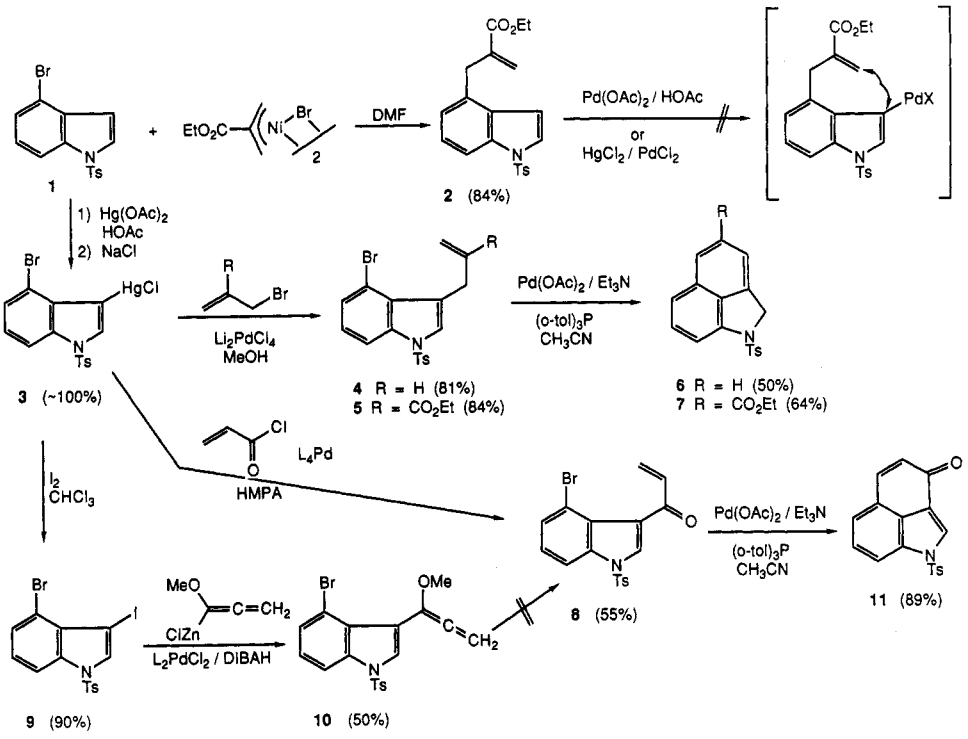
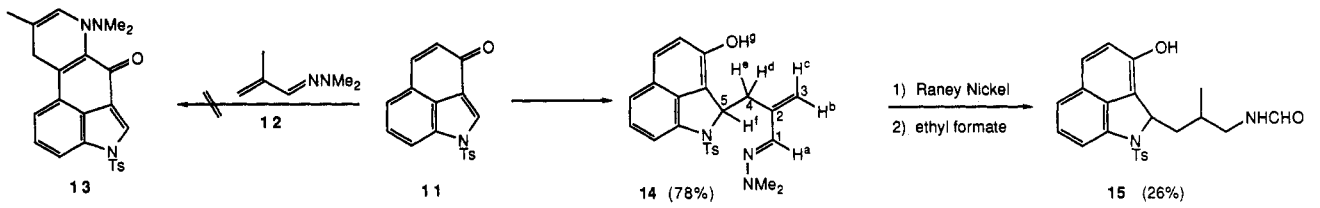
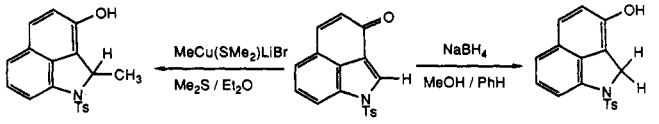
Scheme I



Scheme II



evidenced by the reactions with sodium borohydride and with methylcopper (eq 2). Attempts to elaborate the



(2)

indole nucleus to tetracyclic ergot alkaloids have often been complicated by isomerization to naphthalenoid compounds, especially when the indole nitrogen was protected by groups capable of π-overlap with the nitrogen lone pair.[15] Tricyclic enone 11 is no exception. Addition to the 2-position to directly produce the stable naphthol moiety is strongly favored, and precludes further elaboration of 11 to tetracyclic ergot alkaloids.

Experimental Section

General Data. Melting points were taken on a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Beckman 4240 or a Perkin-Elmer 1600 Series FTIR. NMR spectra were recorded with an IBM-Brucker WP270SY (270 MHz for ^{1}H and 67 MHz for ^{13}C NMR), a Nicolet NTC FT1180 (360 MHz), or a Brucker ACE 300 (300 MHz for ^{1}H and 75.5 MHz for ^{13}C NMR, DEPT, and two-dimensional proton–carbon heteronuclear correlation (HETCOR)) spectrophotometer with tetramethylsilane (Me_4Si) as an internal standard. UV/vis spectra were obtained on a Varian DMS 80 spectrophotometer.

For purification of crude reaction mixtures, radial chromatography (Chromatotron Model 7924) or column chromatographic techniques were used in most cases. Merck silica gel 60 PF (radial chromatography), Merck silica gel (230–400 mesh), and Alfa silica gel (70 micron) were used as stationary phases. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Materials. Tetrahydrofuran and diethyl ether were predried over CaH_2 and distilled from benzophenone ketyl under a nitrogen atmosphere prior to use. Hexane and petroleum ether were distilled under atmospheric pressure. Ethyl acetate, methylene chloride, and acetonitrile were distilled from CaH_2. Dimethylformamide and hexamethylphosphoramide were dried over activated 4-Å molecular sieves. Trimethylamine was distilled from solid KOH.

Palladium acetate (Strem), mercury(II) chloride (J. T. Baker), tri-*o*-tolylphosphine (Strem), sodium hydride (Aldrich), sodium borohydride (Alfa), and triphenylphosphine (Aldrich) were obtained from commercial suppliers and used without further purification. Tosyl chloride (J. T. Baker) was recrystallized, and acryloyl chloride (Aldrich) was distilled prior to use.

Copper bromide–dimethyl sulfide complex,[16] π-(2-carbethoxyallyl)nickel bromide,[17] tetrakis(triphenylphosphine)palladium(0),[18] 4-bromo-3-(chloromercurio)-1-tosylindole (**3**),[1] 4-bromo-3-iodo-1-tosylindole (**9**),[1] 1-(*N*,*N*-dimethylamino)-3-methyl-1-aza-1,3-butadiene (**12**),[20] and 4-bromo-3-allyl-1-tosyl-

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indole (4)[1] were prepared by literature methods. 4-Bromo-1-tosylindole (1) was prepared by literature method[1] or by tosylation of 4-bromoindole made according to Rapoport.[19] Lithium tetrachloropalladate (0.1 M) was prepared by refluxing a suspension of $PdCl_2$ (0.885 g, 5.00 mmol) and LiCl (0.424 g, 10.00 mmol) in 50 mL of CH_3OH under argon for 30 min.

4-Bromo-1-tosylindole (1). To a suspension of NaH (0.877 g, 36.5 mmol, used as a 50% oil dispersion washed with hexanes) in 90 mL of DMF under argon at −5 °C was added a solution of 4-bromoindole (6.52 g, 33.2 mmol, prepared according to Rapoport[19]) in 80 mL of DMF over 1.5 h. After the addition was complete, the homogeneous reaction mixture was stirred for 1.5 h at −5 °C. An argon-saturated solution of tosyl chloride (6.33 g, 33.2 mmol) in 90 mL of DMF was added dropwise to the reaction over 1 h, while maintaining the temperature at −5 °C. The reaction was stirred for 2.5 more hours, during which time the temperature rose to 5 °C.

The reaction mixture was combined with 500 mL of ice–water and extracted with five 150-mL portions of ether. The combined organic extracts were washed with 150 mL of water and 150 mL of saturated NaCl solution and dried over $MgSO_4$. Removal of solvent under reduced pressure yielded a tan solid. Recrystallization from hexanes yielded 4-bromo-1-tosylindole (1) (7.82 g, 22.3 mmol, 67%) as white crystals: mp 120–122 °C (lit.[1] mp 119–121 °C).

4-(2-Carbethoxyprop-2-enyl)-1-tosylindole (2). π-(2-Carbethoxyallyl)nickel bromide (0.56 g, 1.3 allyl equiv) was transferred in a nitrogen-filled glovebag to a tared 100-mL one-necked flask with a sidearm stopcock, capped with a serum cap and containing a magnetic stirring bar. 4-Bromo-1-tosylindole (0.62 g, 1.78 mmol) was dissolved in 10 mL of distilled DMF, degassed, and put under argon. This colorless solution was then transferred to the flask containing the π-(2-carbethoxyallyl)nickel bromide[15] using a cannula with positive argon pressure, and the resulting dark red solution was stirred at room temperature for 10–12 h. The reaction mixture was taken up in 200 mL of ether, which was then washed with three 100-mL portions of H_2O. The organic layer was then dried over $MgSO_4$ and evaporated, providing a yellow oil. After purification by radial chromatography (1:1 hexane/ether), compound 2 was isolated as a colorless oil (0.58 g, 84%): ^1H NMR (360 MHz, $CDCl_3$) δ 1.22 (t, 3 H, OCH_2CH_3, J = 7.2 Hz), 2.34 (s, 3 H, CH_3), 3.81 (s, 2 H, CH_2), 4.17 (q, 2 H, OCH_2CH_3, J = 7.2 Hz), 5.30 (s, 1 H, =CH), 6.20 (s, 1 H, =CH), 6.67 (d, 1 H, indole-3*H*, J = 3.6 Hz), 7.05 (d, 1 H, ArH, J = 8.6 Hz), 7.22 (d, 2 H, TsH, J = 8.3 Hz), 7.22 (d, 1 H, ArH, J = 8.6 Hz), 7.40 (d, 1 H, indole-2*H*, J = 3.6 Hz), 7.76 (d, 2 H, TsH, J = 8.3 Hz), 7.86 (d, 1 H, ArH, J = 8.6 Hz); IR (CCl_4) ν 3150, 3020, 1720(CO), 1636, 1604, 1534, 1489, 1375, 1282, 1178, 1165, 1130, 1092, 1027, 957 cm^{-1}. Anal. Calcd for $C_{21}H_{21}NSO_4$: C, 65.80; H, 5.48; N, 3.65. Found: C, 65.61; H, 5.46; N, 3.56.

4-Bromo-3-(2-carbethoxyprop-2-enyl)-1-tosylindole (5). 4-Bromo-3-(chloromercurio)-1-tosylindole (3) (0.20 g, 0.34 mmol) and 2-carbethoxyallyl bromide (0.66 g, 3.4 mmol) were mixed in 7 mL of MeOH. Li_2PdCl_4 (0.69 mL of a 0.1 M MeOH solution) was then added, and the brown solution was stirred for 72 h at room temperature. The MeOH was then removed under reduced pressure, and the resulting dark red oil was filtered through a short silica gel column using 1:1 petroleum ether/ether as eluent. The residue was further purified by radial chromatography (3:1 petroleum ether/ether, R_f = 0.26). A colorless oil (0.13 g, 84%) was obtained: ^1H NMR (360 MHz, $CDCl_3$) δ 1.30 (t, 3 H, OCH_2CH_3, J = 7.1 Hz), 2.35 (s, 3 H, CH_3), 3.93 (s, 2 H, CH_2), 4.24 (q, 2 H, OCH_2CH_3, J = 7.1 Hz), 5.22 (d, 1 H, CH, J = 1.0 Hz), 6.24 (d, 1 H, CH, J = 1.0 Hz), 7.12 (t, 1 H, ArH, J = 8.1 Hz), 7.22 (d, 2 H, TsH, J = 8.2 Hz), 7.36 (dd, 1 H, ArH, J = 7.8, 0.7 Hz), 7.39 (s, 1 H, indole-2*H*), 7.71 (d, 2 H, TsH, J = 8.2 Hz), 7.96 (dd, 1 H, ArH, J = 7.8, 0.7 Hz). This material was used without further purification, being converted to 1-tosylbenz[*cd*]indoline (6) by a previously reported procedure.[1]

4-Carbethoxy-1-tosylbenz[*cd*]indoline (7). 4-Bromo-3-(2-carbethoxyprop-2-enyl)-1-tosylindole (0.16 g, 0.35 mmol) (5), palladium acetate (0.004 g, 0.02 mmol), tri-*o*-tolylphosphine (0.016 g, 0.053 mmol), and triethylamine (0.072 g, 0.71 mmol) were combined in 3 mL of MeCN in a 5-mL acylation tube. The tube was flushed with argon, sealed, and heated to 100 °C for 24 h. The reaction mixture was diluted with 25 mL of methylene chloride and filtered through Celite. An orange residue remained after removing the solvent in vacuo, and it was further purified by radial chromatography (3:1 petroleum ether/ether, R_f = 0.13). The colorless solid product was then recrystallized from 50 mL of hexane (86.4 mg, 64%): mp 146–147 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.41 (t, 3 H, OCH_2CH_3, J = 7.1 Hz), 2.32 (s, 3 H, CH_3), 4.40 (q, 2 H, OCH_2CH_3, J = 7.1 Hz), 5.18 (s, 2 H, CH_2), 7.22 (d, 2 H, TsH, J = 8.2 Hz), 7.43–7.54 (m, 3 H, ArH), 7.78 (d, 2 H, TsH, J = 8.2 Hz), 7.79 (s, 1 H, ArH), 8.36 (s, 1 H, ArH); IR (KBr) ν 3070, 2995, 2940, 1715(CO), 1623, 1607, 1496, 1456, 1375, 1362, 1298, 1218, 1185, 1168, 1138, 1080, 1027 cm^{-1}. Anal. Calcd for $C_{21}H_{19}NSO_4$: C, 66.07; H, 4.98; N, 3.67. Found: C, 66.22; H, 5.04; N, 3.55.

4-Bromo-3-acryloyl-1-tosylindole (8). A 250-mL airless flask fitted with a reflux condensor capped with a rubber septum was charged with 4-bromo-3-(chloromercurio)-1-tosylindole (3) (5.84 g, 9.37 mmol), acryloyl chloride (1.70 g, 18.74 mmol), tetrakis(triphenylphosphine)palladium(0) (0.10 g, 0.09 mmol), HMPA (110 mL), and a stir magnet. The flask was flushed with argon and heated to 85 °C for 2 h. The reaction mixture was cooled to room temperature, opened to the atmosphere, and more $Pd(PPh_3)_4$ (0.075 g, 0.065 mmol, 1.6 mol % total palladium) was added. Again the flask was flushed with argon and heated to 85 °C for 4 h. After cooling to room temperature the reaction mixture was added to 1 L of H_2O and extracted with four 250-mL portions of ether. The combined ether extracts were washed with 500 mL each of saturated $NaHCO_3$ solution, 3 M $Na_2S_2O_3$ solution, 0.1 N HCl solution, water, and saturated NaCl solution and dried over $MgSO_4$. Filtration followed by removal of solvent under reduced pressure left a tan solid. Purification of the crude material by silica gel chromatography using 30% ether in hexanes as eluent gave 8 (2.07 g, 5.12 mmol, 55%) as a white solid: mp 141–143 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 2.35 (s, 3 H, CH_3), 6.06 (dd, 1 H, J = 0.9, 10.4 Hz, =CH_2), 6.20 (dd, 1 H, J = 0.9, 17.2 Hz, =CH_2), 6.80 (dd, 1 H, J = 10.4, 17.2 Hz, =CH), 7.16–7.34 (m, 3 H, TsH, ArH), 7.47 (d, 1 H, ArH, J = 7.7 Hz), 7.79 (d, 2 H, TsH, J = 8.4 Hz), 7.94 (s, 1 H, indole-2*H*), 7.98 (d, 1 H, ArH, J = 8.3 Hz); ^{13}C NMR (67 MHz, $CDCl_3$) δ 21.36 ($TsCH_3$), 112.57 (=C), 113.21 (=C), 125.58, 126.31, 126.84, 127.05, 127.96, 128.90, 129.53, 129.91, 130.17, 130.49, 137.98, 145.82, 206.45 (CO); IR (KBr) ν 3140, 2930, 1669(CO), 1620, 1602, 1562, 1535, 1500, 1468, 1420, 1410, 1380, 1312, 1300, 1200, 1181, 1170, 1095 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_3NSBr$: C, 53.48; H, 3.49; N, 3.46. Found: C, 53.70; H, 3.61; N, 3.48.

4-Bromo-3-(1-methoxy-1,2-propadienyl)-1-tosylindole (10). A solution of 1-methoxy-1,2-propadiene (0.14 g, 2.0 mmol) and TMEDA (0.46 g, 4.0 mmol) in 10 mL of THF was cooled to −78 °C, and *tert*-butyllithium (2.0 mmol) was then added dropwise. The solution was warmed to −40 °C over a 30-min period, and $ZnCl_2$ (3 mL of a 1 M THF solution) was added. This colorless solutions was stirred at −40 °C for 5 min, after which time the cold bath was removed, and the solution was stirred for 30 min at ambient temperature. The Pd(0) catalyst solution (0.05 mmol, prepared as described below) was then added by cannula. 4-Bromo-3-iodo-1-tosylindole (0.23 g, 0.48 mmol), dissolved in 5 mL of THF, was then added also by cannula. After stirring for 16 h, the reaction mixture was shaken with 5% HCl, extracted with ether, washed with saturated NaCl, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The resulting oil was purified by radial chromatography (R_f = 0.3, 2:1 hexane/ether). A yellow oil (0.10 g, 50%) was isolated. This material was used without further purification: ^1H NMR (270 MHz, $CDCl_3$) δ 2.30 (s, 3 H, CH_3), 3.45 (s, 3 H, OCH_3), 4.37 (s, 2 H, =CH_2), 7.22 (d, 2 H, TsH, J = 8 Hz), 7.25 (m, 1 H, ArH), 7.33 (s, 1 H, ArH), 7.62 (d, 1 H, ArH, J = 4 Hz), 7.78 (d, 2 H, TsH, J = 8 Hz), 7.96 (d, 1 H, ArH, J = 3.5 Hz); IR ($CDCl_3$) ν 3010, 2950, 2896, 1900, 1640, 1582, 1519, 1432, 1360, 1157, 1110, 1082, 890 cm^{-1}; mass spectrum (EI) m/e 418, 416 (M^+). **Preparation of the Pd(0) Catalyst Solution.** $PdCl_2(PPh_3)_2$ (0.035 g, 0.05 mmol) was placed in a flask, which was then degassed and filled with argon. THF (10 mL) was added, giving a yellow suspension. Diisobutylaluminum

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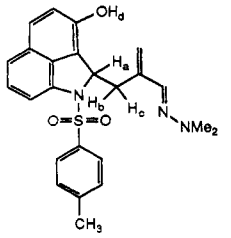
Table I. NOE Data for 14



irradiate	enhancement
H_a	H_b, H_c = 8%, H_d = 5%
H_b	H_c = 37%, H_a = 11%, H_d = 11%
H_c	H_b = 34%, H_a = 14%, H_d = 1%

hydride (0.1 mmol, 0.1 mL of a 1 M hexane solution) was then added, and a dark brown homogeneous solution was formed immediately.

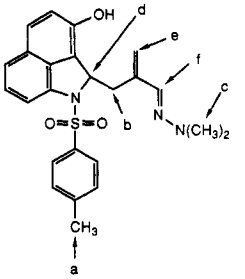
1-Tosyl-3-oxo-1,3-dihydrobenz[*cd*]indoline (11). A 500-mL airless flask fitted with a reflux condenser capped with a rubber septum was charged with 4-bromo-3-acryloyl-1-tosylindole (**8**) (2.07 g, 5.12 mmol), triethylamine (1.03 g, 10.2 mmol, 200 mol %), tri-*o*-tolylphosphine (0.233 g, 0.768 mmol, 15 mol %), palladium(II) acetate (0.05 g, 0.22 mmol), and acetonitrile (350 mL). The flask was flushed with argon and heated at 85 °C for 2 h in an oil bath. After cooling to room temperature, another 0.05 g $Pd(OAc)_2$ was added to the reaction mixture. The flask was again flushed with argon, and heated to 85 °C for 2 more hours.

After cooling, the solvent was removed under reduced pressure, leaving a black-yellow solid. Purification by silica gel chromatography (3:1 hexane/EtOAc, R_f = 0.18) yielded 1.48 g of **11** (4.57 mmol, 89%) as a bright yellow solid: mp 155 °C dec; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.38 (s, 3 H, CH_3), 6.56 (d, 1 H, =CH, J = 9.8 Hz), 7.30 (d, 2 H, TsH, J = 8.2 Hz), 7.49 (m, 2 H, ArH), 7.64 (d, 1 H, =CH, J = 9.8 Hz), 7.88 (d, 2 H, TsH, J = 8.2 Hz), 8.02 (dd, 1 H, ArH, J = 1.5, 7.3 Hz), 8.44 (s, 1 H, indole-2*H*); ^{13}C NMR (67 MHz, $CDCl_3$) δ 21.45 (CH_3), 115.76 (=C), 118.30 (=C), 123.94, 124.41, 126.38, 127.10, 127.23, 130.23, 130.48, 131.84, 132.12, 134.42, 138.85, 146.19, 181.92 (CO); IR (KBr) ν 3116, 3050, 3028, 2920, 1735 (CO), 1649, 1621, 1608, 1595, 1545, 1530, 1439, 1412, 1380, 1365, 1300, 1178, 1141 cm^{-1}. Anal. Calcd for $C_{18}H_{13}NSO_3$: C, 66.86; H, 4.05; N, 4.33. Found: C, 66.81; H, 4.13; N, 4.25.

Aza Diene Adduct (14). 1-Tosyl-3-oxo-1,3-dihydrobenz-[*cd*]indoline (**11**) (0.123 g, 0.381 mmol) and 0.200 mL of 1-(*N*,*N*-dimethylamino)-3-methyl-1-aza-1,3-butadiene were combined, flushed with argon, and stirred at room temperature for 6 h. Removal of excess aza diene under reduced pressure yielded a brown solid. Purification of the crude material by silica gel chromatography (1:1 hexane/Et_2O, R_f = 0.10) yielded **14** (0.128 g, 0.296 mmol, 78%) as a colorless solid: mp 135–136 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.24 (s, 3 H, $TsCH_3$), 2.93 (s, 6 H, $N(CH_3)_2$), 3.13 (dd, 1 H, CH*H*, J = 5.2, 15.3 Hz), 3.30 (br d, 1 H, C*H*H, J = 15.3 Hz), 5.41 (br s, 1 H, =CH*H*), 5.55 (dd, 1 H, CH, J = 5.2, 2.7 Hz), 5.61 (br s, 1 H, =C*H*H), 7.03–7.10 (m, 3 H, ArH, TsH), 7.18 (br s, 1 H, N=C*H*), 7.23–7.35 (m, 2 H, ArH), 7.48 (d, 1 H, ArH, J = 3.3 Hz), 7.50 (d, 1 H, ArH, J = 5.12 Hz), 7.57 (d, 2 H, TsH, J = 8.3 Hz), 8.83 (s, 1 H, ArOH). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.43, 39.57, 42.96, 66.73, 109.33, 119.74, 120.62, 121.63, 122.41, 125.76, 125.78, 126.17, 127.21, 129.54, 130.76, 134.31, 139.42, 140.34, 141.08, 144.01, 147.40; UV (methanol) λ_{max} 232 (ϵ 6000), 285, 342 nm; UV (methanol + 1 drop concentrated aqueous NaOH) λ_{max} 213 (ϵ 7000), 244, 292, 368 nm; IR (film) 3420 (br, OH), 2975, 1609, 1561, 1380, 1168 cm^{-1}; mass spectrum (EI), *m/e* 323 (P – aza diene), 324. Anal. Calcd for $C_{24}H_{25}N_3SO_3$: C, 66.49; H, 5.35; N, 9.69. Found: C, 66.33; H, 5.59; N, 9.60.

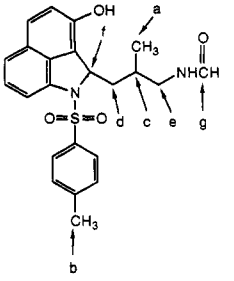
Reduction and N-Formylation of 14 To Produce 15. To a suspension of tricyclic aza diene adduct (**13**) (0.802 g, 0.929 mmol) in 5 mL of MeOH and 5 mL of 1 M KOH was added 2.0 g of aluminum–nickel catalyst (Aldrich) portionwise over 1.5 h.[14] After an additional 40 h of stirring at room temperature, the reaction mixture was diluted with 30 mL of H_2O and 30 mL of CH_2Cl_2 and filtered through Celite. The filtrate was diluted with 50 mL of H_2O, and the aqueous and organic layers were separated. The aqueous layer was extracted with two 100-mL portions of CH_2Cl_2. The combined organic extracts were washed with 100 mL each of water and saturated NaCl solution, dried over $MgSO_4$, and filtered, and solvent was removed under reduced pressure, leaving 0.256 g of crude tan solid.

Table II. Carbon-Proton Correlation Obtained from HETCOR



carbon	^{13}C chemical shift (ppm)	^{1}H chemical shift (ppm)
a	21.43 (q, J = 126.7 Hz)	2.24 (s, 3 H)
b	39.57 (t, J = 122.2 Hz)	3.13 (dd, 1 H, J = 5.2, 15.3 Hz)
		3.30 (br d, 1 H, J = 15.3 Hz)
c	42.96 (q, J = 132.1 Hz)	2.93 (s, 6 H)
d	66.73 (d, J = 146.3 Hz)	5.55 (dd, 1 H, J = 5.2, 2.7 Hz)
e	122.41 (t, J = 158.4 Hz)	5.41 (br s, 1 H)
		4.47 (dd, 1 H, J = 8.0, 14.1 Hz)
		5.61 (br s, 1 H)
f	139.42 (m)	7.18 (br s, 1 H)

Table III. Carbon-Proton Correlation from HETCOR



carbon	^{13}C chemical shift (ppm)	^{1}H chemical shift (ppm)
a	18.63	0.91 (d, 3 H, J = 11.1 Hz)
b	21.39	2.20 (s, 3 H)
c	29.49	2.58–2.67 (m, 1 H)
d	39.97	1.41–1.54 (m, 1 H)
		1.62–1.83 (m, 1 H)
e	42.15	3.04 (dt, 1 H, J = 3.0, 14.0 Hz)
		4.47 (dd, 1 H, J = 8.0, 14.1 Hz)
f	65.69	5.99 (d, 1 H, J = 10.3 Hz)
g	164.29	8.98 (s, 1 H)

The crude material was dissolved in 20 mL of ethyl formate and heated to reflux overnight. Removal of the ethyl formate under reduced pressure gave 0.260 g of a crude brown solid. Purification by radial chromatography (1 mm SiO_2, 4% MeOH in Et_2O, R_f = 0.28) yielded 102 mg of **15** (0.241 mmol, 26%) as a white solid: mp 113–116 °C. This material was relatively unstable and was never obtained in analytically pure form: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (d, 3 H, CH_3, J = 11.1 Hz), 1.41–1.54 (m, 1 H, CH*H*), 1.62–1.83 (m, 1 H, CH*H*), 2.20 (s, 3 H, $TsCH_3$), 2.58–2.76 (m, 1 H, $CH_2CH(CH_3)CH_2$), 3.04 (dt, 1 H, CH*H*NH, J = 3.0, 14.0 Hz), 4.47 (dd, 1 H, J = 8.0, 14.0 Hz, C*H*HNH), 5.99 (d, 1 H, J = 10.2 Hz, CHN), 6.24 (br s, 1 H, NH), 7.00 (m, 3 H, ArH, TsH), 7.26 (t, 1 H, ArH, J = 5.90 Hz), 7.37 (d, 1 H, ArH, J = 8.80), 7.43–7.54 (m, 4 H, TsH, ArH), 8.27 (br s, 1 H, ArOH, vanish with D_2O), 8.38 (s, 1 H, CHO); ^{13}C NMR (75.5 MHz, $CDCl_3$, number of hydrogens assigned by DEPT) δ 18.63 (CH_3), 21.39 ($TsCH_3$), 29.49 (CH), 39.97 (CH_2), 42.15 (CH_2), 65.69 (CH), 111.91 (CH), 119.56 (C), 120.73 (CH), 121.19 (CH), 125.29 (CH), 125.76 (CH), 126.21 (C), 127.13 (CH), 129.41 (CH), 131.98 (C), 133.82 (C), 140.47 (C), 144.00 (C), 147.26 (C), 164.29 (CHO); IR (film) ν 3395, 3264, 3063, 2956, 2921, 2808, 1659 (CO), 1605, 1492, 1380, 1346, 1297, 1160, 1086 cm^{-1}; high-resolution

(FAB) calcd for $C_{23}H_{24}N_2O_4S$ $[M + H]^+$ 425.1535, found 425.1538.

3-Hydroxy-1-tosyl-1,2-dihydrobenz[*cd*]indoline (16). To a solution of 3-oxo-1-tosyl-1,3-dihydrobenz[*cd*]indoline (11) (0.100 g, 0.309 mmol) in 3 mL of benzene/methanol (1:1) at 0 °C was added sodium borohydride (0.023 g, 0.618 mmol). After 1 h, 10 drops of glacial acetic acid was added to the reaction. After 5 additional minutes of stirring, the reaction mixture was diluted with 30 mL of water and extracted with two 30-mL portions of ether. The combined organic extracts were washed with 20 mL each of saturated $NaHCO_3$ solution and saturated NaCl solution, dried over $MgSO_4$, and filtered, and solvent was removed under reduced pressure to give 0.105 g of crude yellow solid. Purification by silica gel flash chromatography (1:1 hexane/Et_2O, R_f = 0.41) yielded **16** (0.090 g, 90%) as a slightly yellow solid: mp 148-149 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3 H, $TsCH_3$), 5.18 (s, 2 H, CH_2), 5.20 (br s, 1 H, ArOH), 6.98 (d, 1 H, ArH, J = 8.6 Hz), 7.21 (d, 2 H, TsH, J = 8.2 Hz), 7.24-7.30 (m, 2 H, ArH), 7.43 (dd, 1 H, ArH, J = 2.4, 5.5 Hz), 7.51 (d, 1 H, ArH, J = 8.7 Hz), 7.78 (d, 2 H, TsH, J = 8.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$, number of vicinal hydrogens assigned by DEPT) δ 21.48 (CH_3), 54.33 (CH_2), 107.03 (*C*H), 116.03 (C), 118.69 (*C*H), 119.76 (*C*H), 125.73 (*C*H), 126.38 (*C*H), 126.94 (C), 127.13 (*C*H), 129.85 (*C*H), 131.97 (C), 134.43 (C), 141.88 (C), 144.32 (C), 145.83 (C); UV (MeOH) λ_{max} 225 (ϵ 7500), 300, 342 nm. UV (MeOH + 1 drop concentrated aqueous NaOH) 211, 225, 302, 363 nm; IR (film) ν 3435 (OH), 2956, 2921, 2853, 1610, 1494, 1374, 1299, 1159, 1121, 1087 cm^{-1}; mass spectrum (EI) m/e 325 (parent). Anal. Calcd for $C_{18}H_{15}NO_3S$: C, 66.44; H, 4.65; N, 4.30. Found: C, 66.54; H, 4.84; N, 4.31.

3-Hydroxy-2-methyl-1-tosyl-1,2-dihydrobenz[*cd*]indoline (17). To a stirred suspension of copper bromide-dimethyl sulfide complex (0.127 g, 0.620 mmol) in 2.4 mL of dimethyl sulfide/diethyl ether (1:1 v/v) under argon at -45 °C was added methyllithium (0.87 mL of 1.4 M solution in ether, 0.620 mmol) dropwise via syringe. The suspension turned yellow immediately. After 3 h, a solution of tricyclic enone (11) (0.100 g, 0.310 mmol) in 2.5 mL of THF was added dropwise to the -45 °C suspension. After 3 h the mixture had warmed to -10 °C. The still cold mixture was diluted with 25 mL of 10% ammonium hydroxide in saturated ammonium chloride and extracted with three 25-mL portions of diethyl ether. Drying the combined organic extracts over $MgSO_4$, filtering, and removal of solvent under reduced pressure left a tan solid. Purification of the crude material by preparative TLC eluted with hexane/ethyl acetate (3:1) yielded indoline **17** (0.05 g, 0.155 mmol, 50%) as a slightly yellow solid: mp 117-120 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.89 (d, 3 H, CH_3, J = 6.4 Hz), 2.29 (s, 3 H, $TsCH_3$), 5.14 (br s, 1 H, ArOH), 5.51 (q, 1 H, CH, J = 6.4 Hz), 6.97 (d, 1 H, ArH, J = 8.6 Hz), 7.15 (d, 2 H, TsH, J = 8.3 Hz), 7.23-7.34 (m, 2 H, ArH), 7.42-7.52 (m, 2 H, ArH), 7.73 (d, 2 H, TsH, J = 8.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$, number of hydrogens assigned by DEPT) δ 21.30 (CH_3), 21.44 (CH_3), 64.27 (*C*H), 108.49 (*C*H), 119.21 (*C*H), 119.99 (*C*H), 121.71 (C), 125.67 (*C*H), 126.38 (*C*H), 126.76 (C), 127.11 (*C*H), 129.67 (*C*H), 134.81 (C), 141.32 (C), 144.05 (C), 145.98 (C), 148.01 (C); IR (film) ν 3429 (OH), 3060, 2976, 2920, 1641, 1610, 1496, 1371, 1346, 1284, 1162 cm^{-1}; mass spectrum (EI) m/e 339 (parent). Anal. Calcd for $C_{19}H_{17}NO_3S$: C, 67.24; H, 5.05; N, 4.13. Found: C, 67.40; H, 5.20; N, 3.92.

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Preparation of Allenic Sulfones and Allenes from the Selenosulfonation of Acetylenes

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β-(Phenylseleno)vinyl sulfones **2** are readily obtained from the free-radical selenosulfonation of acetylenes. Compounds **2** isomerize to allyl sulfones **4** under base-catalyzed conditions in nearly quantitative yield, with high stereoselectivity favoring the *Z* configuration. Allyl sulfones **4** afford generally high yields of allenic sulfones **1** when subjected to oxidation with *m*-chloroperbenzoic acid or *tert*-butyl hydroperoxide, followed by selenoxide syn-elimination. The sulfone-stabilized anion intermediates in the isomerizations of **2** to **4** can be alkylated, deuterated, or silylated in the α-position prior to oxidation, providing allenic sulfones with an additional α-substituent. In some cases, spontaneous elimination of the phenylseleno group occurred, producing the allenic sulfone without the need for an oxidation step. Desulfonylation of allyl sulfones **4f**, **4c**, and **25** with sodium amalgam afforded vinyl selenides that were converted to allenes in moderate to good yields by oxidation-elimination. The copper-catalyzed coupling of allyl sulfones **4** with Grignard reagents comprises an alternative route to vinyl selenide precursors of allenes. These procedures permit the syntheis of various α- and γ-substituted allenic sulfones and allenes from acetylenes.

Allenic sulfones **1** are of increasing importance in organic synthesis, particularly as dienophiles[1] and dipolarophiles[2] in cycloadditions,[3] and in addition reactions with various nucleophiles.[4] They are typically prepared by the isomerization of propargyllic sulfones,[4f] from the oxidation of allenic sulfides or sulfoxides,[5] by the rearrangement of

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