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Conjugate Additions, Aza-Cope, and Dissociative Rearrangements and Unexpected Electrocyclic Ring Closures in the Reactions of 2-(2-Pyrrolidinyl)-Substituted Heteroaromatic Systems with Acetylenic Sulfones

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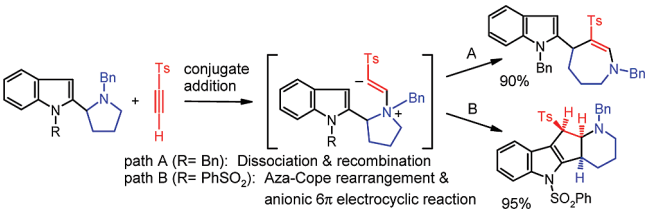

The reactions of 2-heteroaryl-substituted pyrrolidines with acetylenic sulfones proceeded via two pathways. The first involves conjugate addition of the pyrrolidine to the acetylenic sulfone to afford a zwitterion, followed by dissociation of the C−N bond and recombination of the resulting carbocation and vinyl anion to afford the corresponding azepine derivative. The second comprises a cascade of conjugate addition, aza-Cope rearrangement and anionic 6π electrocyclic ring-closure steps. The stability of the carbocation intermediate formed by C−N cleavage determines the dominant pathway.

The 3-aza-Cope rearrangement provides a potentially useful method for the conversion of *N*-allyl-substituted enamines to the corresponding imines.[1,2] A limitation of such processes is their typically high activation energies, which result in the requirement for strongly elevated temperatures. Fortunately, quaternization of the amino group lowers the activation energy substantially and enhances the synthetic value of the reaction. This may be achieved by *N*-alkylation, protonation, or coordination of the nitrogen atom with Lewis acids.[3]

We recently demonstrated that a variety of tertiary cyclic α-vinyl amines or acyclic allyl amines undergo conjugate additions to acetylenic sulfones **1**,[4] followed by formal aza-Cope rearrangements of the resulting zwitterions **2**.[5,6] Because the rearrangement step is accompanied by the cancellation of charge in the zwitterion, these reactions proved exceptionally facile and proceeded at temperatures between −78 and 40 °C. When cyclic α-vinyl amines were used, the overall process resulted in ring-expansion of the original amine by four carbon atoms to afford products **3**, containing rings ranging in size from 9 to 17 members (Scheme 1).[5] An extension to the ring-expansion of α-vinyl azetidines was subsequently reported by Couty et al.,[7] while an iterative variation of this process was used in the synthesis of the macrocyclic amines motuporamine A and B in our laboratory.[5b] Several related studies of the reactions of tertiary allyl amines with DMAD and other acetylenic esters have also been reported.[8]

Two examples of anomalous behavior were observed during our previous investigation.[5b] In the first, the zwitterion derived from an α-vinyl aziridine underwent ring-opening of the strained aziridinium ion by methanol instead of the usual aza-Cope rearrangement (Scheme 2). In the second, a dissociative mechanism predominated, wherein a methoxy-stabilized allyl carbocation was formed by C−N bond cleavage (Scheme 3). In contrast, Hassner et al. reported that vinyl aziridines undergo rearrangements with ring-expansion when reacted with various other activated acetylenes and alkenes,[9] while Lindström and Somfai[2k] observed [3,3]-aza-Claisen enolate rearrangements of amides of vinyl aziridines. Previous examples of C−N bond cleavage that followed the initial

(1) For reviews, see: (a) Nubbemeyer, U. *Top. Curr. Chem.* **2005**, *244*, 149–213. (b) Enders, D.; Knopp, M.; Schiffers, R. *Tetrahedron: Asymmetry* **1996**, *7*, 1847–1882. (c) Blechert, S. *Synthesis* **1989**, 71–82. (d) Przheval'skii, N. M.; Grandberg, I. I. *Russ. Chem. Rev.* **1987**, *56*, 477–491. (e) Lutz, R. P. *Chem. Rev.* **1984**, *84*, 205–246.

(2) For recent examples, see: (a) Waetzig, S. R.; Tunge, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 4138–4139. (b) Craig, D.; King, N. P.; Mountford, D. M. *Chem. Commun.* **2007**, 1077–1079. (c) Hemming, K.; O'Gorman, P. A.; Page, M. I. *Tetrahedron Lett.* **2006**, *47*, 425–428. (d) Fiedler, D.; van Halbeek, H.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2006**, *128*, 10240–10252. (e) Fiedler, D.; Bergman, R. G.; Raymond, K. N. *Angew. Chem., Int. Ed.* **2004**, *43*, 6748–6751. (f) Zheng, J.-F.; Jin, L.-R.; Huang, P.-Q. *Org. Lett.* **2004**, *6*, 1139–1142. (g) Davies, S. G.; Garner, A. C.; Nicholson, R. L.; Osborne, J.; Savory, E. D.; Smith, A. D. *Chem. Commun.* **2003**, 2134–2135. (h) Winter, R. F.; Rauhut, G. *Chem.—Eur. J.* **2002**, *8*, 641–649. (i) Gomes, M. J. S.; Sharma, L.; Prabhakar, S.; Lobo, A. M.; Glória, P. M. C. *Chem. Commun.* **2002**, 746–747. (j) Cardoso, A. S.; Lobo, A. M.; Prabhakar, S. *Tetrahedron Lett.* **2000**, *41*, 3611–3613. (k) Lindström, U. M.; Somfai, P. *Chem.—Eur. J.* **2001**, *7*, 94–98. (l) McComsey, D. F.; Maryanoff, B. E. *J. Org. Chem.* **2000**, *65*, 4938–4943. (m) Suh, Y.-G.; Kim, S.-A.; Jung, J.-K.; Shin, D.-Y.; Min, K.-H.; Koo, B.-A.; Kim, H.-S. *Angew. Chem., Int. Ed.* **1999**, *38*, 3545–3547. (n) For a related example of a 1-aza-Cope rearrangement (formally the reverse of a 3-aza-Cope process), see: Kang, J.; Kim, T. H.; Yew, K. H.; Lee, W. K. *Tetrahedron: Asymmetry* **2003**, *14*, 415–418.

(3) Walters, M. A. *J. Org. Chem.* **1996**, *61*, 978−983 and refs cited therein.

(4) For reviews of acetylenic sulfones, see: (a) Back, T. G. *Tetrahedron* **2001**, *57*, 5263–5301. (b) Back, T. G.; Clary, K. N.; Gao, D. *Chem. Rev.* **2010**, DOI: 10.1021/cr1000546.

(5) (a) Weston, M. H.; Nakajima, K.; Parvez, M.; Back, T. G. *Chem. Commun.* **2006**, 3903–3905. (b) Weston, M. H.; Nakajima, K.; Back, T. G. *J. Org. Chem.* **2008**, *73*, 4630–4637.

(6) Although we refer to these processes as formal 3-aza-Cope rearrangements, it is possible that they proceed via intramolecular S_N' displacements of the quaternary nitrogen by the sulfone-stabilized vinyl anion in the zwitterion intermediates.

(7) Drouillat, B.; Couty, F.; Razafimahaléo, V. *Synlett* **2009**, 3182–3186.

(8) (a) Kandeel, K. A.; Vernon, J. M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2023–2026. (b) Schwan, A. L.; Warkentin, J. *Can. J. Chem.* **1988**, *66*, 1686–1694. (c) Baxter, E. W.; Labaree, D.; Ammon, H. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 7682–7692. (d) Vedejs, E.; Gingras, M. *J. Am. Chem. Soc.* **1994**, *116*, 579–588.

(9) (a) Hassner, A.; D'Costa, R.; McPhail, A. T.; Butler, W. *Tetrahedron Lett.* **1981**, *22*, 3691–3694. (b) Hassner, A.; Chau, W.; D'Costa, R. *Isr. J. Chem.* **1982**, *22*, 76–81.

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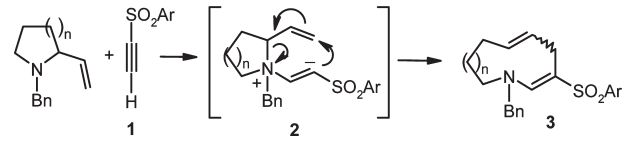
SCHEME 1



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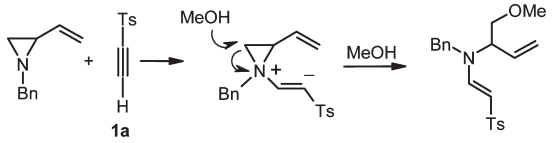

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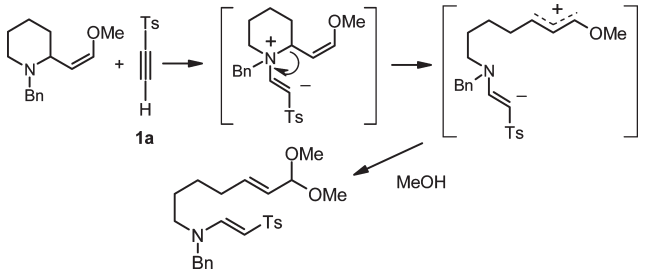

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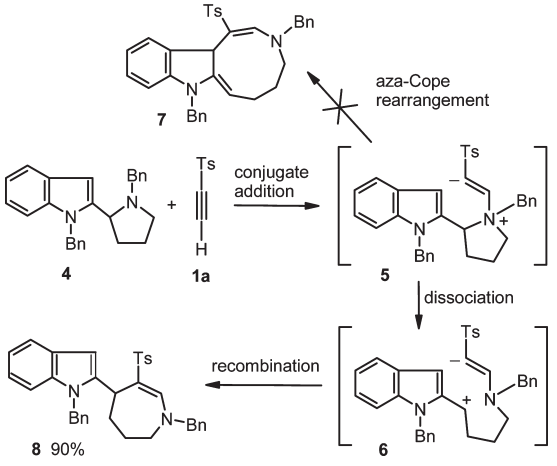


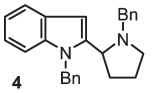
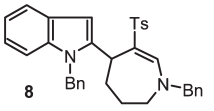
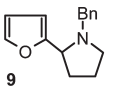
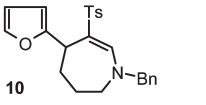
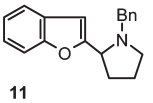
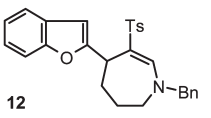
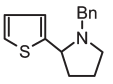
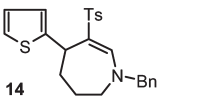
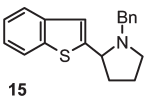
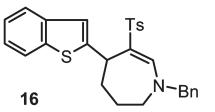
conjugate addition of thebaine derivatives to an allenic sulfone were reported by Kanematsu et al.,[10] while other examples of dissociation during the reactions of allyl amines with variously activated acetylenes were noted by Schwan and Warkentin,[8b] Vedejs and Gingras,[8d] and by Voskressensky et al.[11]

We were also interested in investigating the reactions of acetylenic sulfones with tertiary amines containing α-vinyl groups that are part of aromatic systems to extend the scope

(10) Fujii, I.; Ryu, K.; Hayakawa, K.; Kanematsu, K. *J. Chem. Soc., Chem. Commun.* **1984**, 844–845.

(11) (a) Voskressensky, L. G.; Borisova, T. N.; Listratova, A. V.; Kulikova, L. N.; Titov, A. A.; Varlamov, A. V. *Tetrahedron Lett.* **2006**, *47*, 4585–4589. (b) Voskressensky, L. G.; Listratova, A. V.; Borisova, T. N.; Alexandrov, G. G.; Varlamov, A. V. *Eur. J. Org. Chem.* **2007**, 6106–6117. (c) Voskressensky, L. G.; Listratova, A. V.; Borisova, T. N.; Kovaleva, S. A.; Borisov, R. S.; Varlamov, A. V. *Tetrahedron* **2008**, *64*, 10443–10452.

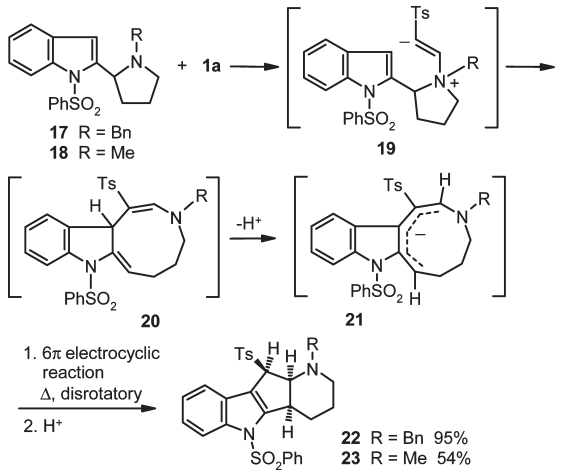
TABLE 1. Reactions of 2-(2-*N*-Benzylpyrrolidyl)-Substituted Heteroaromatic Compounds with Acetylenic Sulfone 1a

entry	starting material	product	isolated yields (%)
1			90
2			70
3			91
4			98
5			51

of these processes further. We now report that the reaction of 1-benzyl-2-(1-benzylpyrrolidin-2-yl)-1*H*-indole (**4**) with (*p*-toluenesulfonyl)ethyne (**1a**) proceeded smoothly at room temperature in acetonitrile, affording the tetrahydroazepine **8** in 90% yield, instead of the aza-Cope product **7**. This is consistent with the expected conjugate addition of **4** to **1a**, followed by dissociation of the C−N bond in the resulting zwitterion **5**, to produce the resonance-stabilized cation **6**. Recombination of the cation with the sulfone-stabilized vinyl anion then afforded the azepine **8** instead of the corresponding tetrahydroazonine **7**, the expected product of a formal aza-Cope rearrangement (Scheme 4 and entry 1 of Table 1). The formation of **8** instead of **7** is attributed to the relatively high stability of the carbocation **6** and the partial loss of aromaticity of the indole moiety in the formation of **7**. The reactions of acetylenic sulfone **1a** with the corresponding furan, benzofuran, thiophene, and benzothiophene derivatives **9**, **11**, **13**, and **15**, respectively, were performed under similar conditions, affording the analogous tetrahydroazepine products **10**, **12**, **14**, and **16**, respectively, in generally high yield (Table 1, entries 2−5). The structure of the furan derivative **10** was established conclusively by 2D NMR methods, including COSY, HSQC, and HMBC, while that of **8** was confirmed by X-ray diffraction (see Supporting Information).

To our surprise, when the indole *N*-benzyl group of **4** was replaced with the electron-withdrawing benzenesulfonyl substituent and the reaction of the resulting indole derivative **17** with **1a** was repeated under the same conditions, a completely different product **22** was isolated in 95% yield (Scheme 5). The indicated tetracyclic structure and stereochemistry of **22** were confirmed by X-ray diffraction (see Supporting Information). The analogous tetracyclic product **23** was obtained similarly, albeit in lower yield, when the pyrrolidine *N*-benzyl group was replaced with an *N*-methyl substituent in **18**. Thus, a complete change in reaction pathway was effected by simply switching the indole *N*-benzyl

SCHEME 5

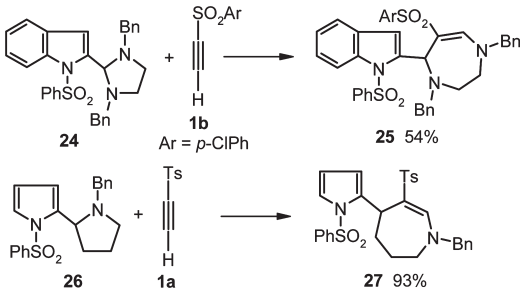


group for the more electron-withdrawing sulfonyl substituent.

We propose that the unexpected formation of the tetracyclic structures **22** and **23** from **17** and **18**, respectively, in Scheme 5 occurs via a cascade of three separate reactions, where the usual conjugate additions produce the expected zwitterions **19**, which then undergo aza-Cope rearrangements to afford tetrahydroazonines **20**, as observed earlier with the α-vinylamines shown in Scheme 1. This is followed by a further cyclization to afford the observed products **22** and **23**. The possibility that the latter proceeds via a transannular conjugate addition of the indole enamine moiety of **20** to the *β*-position of the vinyl sulfone group is unlikely because of the diminished nucleophilicity of the enamine caused by the electron-withdrawing *N*-benzenesulfonyl substituent. A more plausible mechanism is shown in Scheme 5 and is based on the relatively high acidity of the C-3 proton of the indole moiety of **20**, which permits facile deprotonation, followed by an anionic 6*π*-electron electrocyclic ring closure of anions **21**, leading to **22** and **23** after reprotonation.[12] The disrotatory nature of the ground state electrocyclic reaction is consistent with the *cis*-fused cyclopentene and piperidine rings found in the final products. The pyrrolidine or piperidine moieties of the starting material and product, respectively, presumably serve as the required base in the deprotonation step.

In contrast to the above cascade of conjugate addition, aza-Cope rearrangement and electrocyclic ring-closure steps observed with **17** and **18**, replacement of the pyrrolidine moiety of **17** with the cyclic aminal of **24** resulted solely in the formation of the corresponding tetrahydrodiazepine **25** when **24** was treated with the *p*-chlorophenyl-substituted acetylenic sulfone **1b**.[13] Finally, the *N*-(benzenesulfonyl)-pyrrole analogue **26** reacted with **1a** in the same way as *N*-benzylindole **4**, producing tetrahydroazepine **27** (Scheme 6). Thus, all of the heteroaromatic compounds investigated,

SCHEME 6



except **17** and **18**, reacted with acetylenic sulfones **1** via the conjugate addition−dissociation−recombination pathway shown for **4** in Scheme 4.

The remarkable dichotomy of behavior between *N*-(benzenesulfonyl)indoles **17** and **18** and the other compounds studied can be explained on the basis of the relative stabilities of the carbocation moiety of **6**, produced by C−N bond cleavage in the dissociation pathway. The carbocation intermediate required for the dissociation mechanism in the case of **17** and **18** is destabilized by the *N*-benzenesulfonyl group, relative to the cations postulated in the reactions of the otherwise similar *N*-benzylindole derivative **4** (Scheme 4), and in the other reactions summarized in Table 1. This suppresses the rate of the dissociative mechanism and enables the aza-Cope pathway to dominate. On the other hand, in the case of aminal **24**, mesomeric electron donation from the extra nitrogen atom to the corresponding carbocation compensates for the destabilization of the cation by the *N*-benzenesulfonyl group. Thus, the dissociative pathway prevails. The difference in behavior between *N*-(benzenesulfonyl)indole **17** and the analogous pyrrole derivative **26** is more puzzling, but it is worth noting that electrophilic reactions of indoles occur preferentially at the 3-position, while those of pyrroles generally occur at C-2. This is consistent with better stabilization of a carbocation center attached at the 2-position of an adjacent pyrrole ring than at the same position of an indole moiety. The higher stability of the corresponding cation would then account for the greater propensity for the dissociative pathway in pyrrole **26** than in indole **17**, despite the presence of the electron-withdrawing benzenesulfonyl substituent in both compounds.

In conclusion, we have now observed four distinct pathways in the reactions of tertiary amines containing α-vinyl or α-heteroaryl groups with acetylenic sulfones. These all originate from the initial conjugate addition of the amine to the acetylenic sulfone, followed by either the aza-Cope rearrangement and ring-expansion in Scheme 1, the aziridine ring-opening of Scheme 2, the dissociative mechanism resulting in cleavage of the C−N bond followed by either carbocation capture with methanol or recombination, as shown in Schemes 3 and 4, respectively, and the unexpected aza-Cope rearrangement and electrocyclic ring-closure depicted in Scheme 5.

Experimental Section

General Experimental. NMR spectra were recorded in deuteriochloroform and mass spectra were obtained by electron impact, unless otherwise indicated. The preparation and characterization of the starting materials **9**, **11**, **13**, **15**, **18**, **24**, and **26** are described in the Supporting Information. Acetylenic sulfones **1a** and **1b** were prepared by literature methods.[5b,14]

(12) Anionic 6*π*-electron electrocyclic reactions are relatively rare but have been reported previously. For example, the disrotatory ring-closure of the cyclooctadienyl anion produces the corresponding *cis*-fused [3.3.0]bicyclooctene species after protonation, similarly to the present case. See: Bates, R. B.; McCombs, D. A. *Tetrahedron Lett.* **1969**, *10*, 977–978.

(13) The use of **1a** in this experiment produced a more complex mixture of products. Compound **1b** is more electrophilic than **1a** and may facilitate the initial conjugate addition step by better stabilizing the resulting vinyl anion.

Preparation of 1-Benzyl-2-(1-benzylpyrrolidin-2-yl)-1*H*-indole (4). 1-Benzyl-2-(pyrrolidin-2-yl)-1*H*-indole was prepared by a literature method[15] and the pyrrolidine moiety was *N*-benzylated with benzyl bromide-triethylamine in dichloromethane by the same general procedure as in the preparation of **17** (vide infra) to afford **4** in 84% yield: IR (film) 1605, 1453, 1162 cm^{-1}; ^1H NMR (300 MHz) δ 7.74 (m, 1H), 7.38−7.15 (m, 11H), 7.04 (d, J = 8.2 Hz, 2H), 6.76 (s, 1H), 5.94 (d, J = 17.3 Hz, 1H), 5.66 (d, J = 17.3 Hz, 1H), 4.27 (d, J = 13.1 Hz, 1H), 3.86 (t, J = 7.9 Hz, 1H), 3.26 (d, J = 13.1 Hz, 1H), 3.25 (m, 1H), 2.35−2.17 (m, 2H), 2.10−1.80 (m, 3H); ^{13}C NMR (75 MHz) δ 142.0, 139.7, 138.5, 138.3, 128.8, 128.7, 128.2, 128.1, 127.3, 127.0, 126.0, 121.5, 120.5, 119.8, 109.9, 101.3, 62.8, 58.7, 53.4, 47.2, 32.5, 22.7; mass spectrum m/z (%) 366 (M^+, 63), 91 (100). HRMS Calcd for $C_{26}H_{26}N_2$, 366.2096; found, 366.2083.

Reaction of 4 with Acetylenic Sulfone 1a (Typical Procedure). Indole **4** (127 mg, 0.347 mmol) and acetylenic sulfone **1a** (62 mg, 0.34 mmol) were stirred for 14 h at room temperature in 5 mL of acetonitrile. The mixture was concentrated and purified by flash chromatography (15−30% ethyl acetate−hexanes) to afford 167 mg (90%) 1-benzyl-5-(1-benzylindol-2-yl)-6-(*p*-toluenesulfonyl)-2,3,4,5-tetrahydro-1*H*-azepine (**8**) as white solid, mp 161−162 °C (from acetonitrile): IR (film) 1627, 1280, 1134 cm^{-1}; ^1H NMR (400 MHz) δ 7.87 (s, 1H), 7.44−7.16 (m, 11H), 7.12−6.98 (m, 5H), 6.85 (d, J = 8.1 Hz, 2H), 5.97 (s, 1H), 5.32 (d, J = 17.3 Hz, 1H), 5.26 (d, J = 17.3 Hz, 1H), 4.50 (d, J = 15.0 Hz, 1H), 4.40 (d, J = 15.0 Hz, 1H), 4.36 (t, J = 3.6 Hz, 1H), 3.52−3.50 (m, 1H), 2.96−2.91 (m, 1H), 2.13 (s, 3H), 1.74−1.67 (m, 3H) 1.50−1.43 (m, 1H); ^{13}C NMR (75 MHz) δ 149.5, 142.1, 140.3, 139.8, 137.8, 137.3, 137.1, 128.9, 128.68, 128.65, 128.1, 127.6, 127.3, 126.8, 126.1, 121.0, 119.8, 119.4, 109.4, 109.0, 103.6, 63.6, 52.6, 46.5, 35.4, 31.7, 23.5, 21.2; mass spectrum m/z (%) 546 (M^+, 51), 455 (46), 391 (100). HRMS Calcd for $C_{35}H_{34}N_2O_2S$, 546.2341; found, 546.2344.

The preparation and characterization data for the other products in Table 1, as well as for **23**, **25**, and **27**, are provided in the Supporting Information.

Preparation of 1-Benzenesulfonyl-2-(1-benzylpyrrolidin-2-yl)-1*H*-indole (17). *N*-(Benzenesulfonyl)indole[16] (2.00 g, 7.77 mmol) and TMEDA (0.93 g, 8.0 mmol) were dissolved in THF (50 mL), cooled to −78 °C, and *n*-butyllithium (3.11 mL, 2.5 M in hexanes, 7.8 mmol) was added slowly. The red solution was warmed to room temperature over 2 h and was then cooled back to −78 °C. *N*-*t*-Butyloxycarbonyl-2-pyrrolidinone (1.44 g, 7.77 mmol) was added and the mixture was stirred at −78 °C for 1 h and then at room temperature for 1 h. Brine was added and the mixture was extracted with ethyl acetate, dried, and concentrated. The residue was purified by flash chromatography (25% ethyl acetate−hexanes) to give 2.02 g (58%) of [4-(1-benzenesulfonyl-1*H*-indol-2-yl)-4-oxo-butyl]-carbamic acid *tert*-butyl ester as a yellow oil.

Trifluoroacetic acid (1.08 mL, 14.6 mmol) was added dropwise to a solution of the above product (2.02 g, 4.52 mmol) in dichloromethane at 0 °C. The mixture was stirred at 0 °C for 2 h, quenched with saturated $NaHCO_3$ solution, extracted with dichloromethane, dried, concentrated, and purified by flash chromatography (50% ethyl acetate−hexanes) to afford 983 mg (67%) of 1-benzenesulfonyl-2-(4,5-dihydro-3*H*-pyrrol-2-yl)-1*H*-indole as a pale yellow solid. This was dissolved in ethanol (40 mL) and sodium borohydride (3.50 g, 92.5 mmol) was added in portions over 2 d. The mixture was concentrated, dissolved in ethyl acetate, washed with aqueous NaOH, dried, and concentrated to produce crude 1-benzenesulfonyl-2-(pyrrolidin-2-yl)-1*H*-indole, which was dissolved in dichloromethane (25 mL), along with triethylamine (0.84 mL, 6.1 mmol) and benzyl bromide (0.36 mL, 3.0 mmol). The mixture was stirred overnight, washed with saturated $NaHCO_3$ solution, dried, concentrated, and purified via flash chromatography (10% ethyl acetate−hexanes) to afford 695 mg (56%) of **17** as a pale yellow oil: IR (film) 1448, 1371, 1173 cm^{-1}; ^1H NMR (300 MHz) δ 8.25 (d, J = 7.7 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.52−7.19 (m, 11H), 7.02 (s, 1H), 4.30−4.25 (m, 1H), 3.90 (d, J = 13.0 Hz, 1H), 3.18 (d, J = 13.0 Hz, 1H), 3.11−3.08 (m, 1H), 2.55−2.47 (m, 1H), 2.29 (dd, J = 16.7, 8.8 Hz, 1H), 1.90−1.73 (m, 3H); ^{13}C NMR (75 MHz) δ 146.2, 139.8, 139.4, 137.8, 133.7, 129.9, 129.2, 128.5, 128.3, 126.9, 126.2, 124.0, 123.7, 120.7, 114.9, 108.6, 62.5, 59.2, 53.6, 34.4, 23.2; mass spectrum m/z (%) 416 (M^+, 25), 324 (45), 275 (100), 91 (65). HRMS Calcd for $C_{25}H_{24}N_2O_2S$, 416.1559; found, 416.1557.

Reaction of 17 with Acetylenic Sulfone 1a (Typical Procedure). Indole **17** (100 mg, 0.240 mmol) and acetylenic sulfone **1a** (43 mg, 0.24 mmol) were stirred for 24 h at room temperature in 5 mL of acetonitrile. The mixture was concentrated and purified via flash chromatography (15−30% ethyl acetate−hexanes), affording 136 mg (95%) of 5-benzenesulfonyl-1-benzyl-10-(*p*-toluenesulfonyl)-1,2,3,4,4a,5,10,10a-octahydro-pyrido[2′,3′:4,5]-cyclopenta[1,2-*b*]indole (**22**) as a pale yellow solid: mp 132−135 °C (from toluene-hexanes); IR (film) 1596, 1449, 1366, 1184 cm^{-1}; ^1H NMR (300 MHz) δ 7.96 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 7.4 Hz, 2H), 7.56−7.50 (m, 2H), 7.35−7.20 (m, 11H), 6.94 (d, J = 7.9 Hz, 2H), 4.92 (d, J = 4.4 Hz, 1H), 4.30 (dd, J = 7.7, 4.7 Hz, 1H), 4.00 (d, J = 14.0 Hz, 1H), 3.75 (d, J = 13.8 Hz, 1H), 3.73 (m, 1H), 2.64−2.58 (m, 1H), 2.54−2.41 (m, 1H), 2.34 (s, 3H), 2.27−2.15 (m, 1H), 1.88−1.75 (m, 1H), 1.60−1.47 (m, 1H), 1.09−0.95 (m, 1H); ^{13}C NMR (75 MHz) δ 149.5, 144.7, 140.5, 139.6, 138.2, 134.3, 134.1, 129.8, 129.6, 129.6, 128.9, 128.8, 128.7, 127.4, 126.9, 125.0, 124.7, 121.6, 119.5, 115.0, 68.5, 66.5, 59.1, 45.0, 39.3, 25.7, 22.1, 17.6; mass spectrum m/z (%) 455 (100), 209 (50), 91 (46). HRMS Calcd for $C_{28}H_{27}N_2O_2S$ ($M^+ - C_6H_5SO_2$), 455.1793; found, 455.1780.

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Supporting Information Available: Characterization data and ^1H and ^{13}C NMR spectra of new compounds; 2D NMR spectra of **10**; X-ray crystallographic data for **8** and **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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