Metal-Catalyzed Reaction Of Indoline Diazoamides Possessing a C-2 CH_2X Substituent: Site-Selectivity, Diastereoselectivity, and Chemoselectivity

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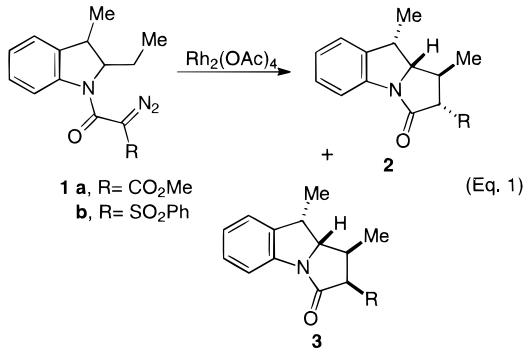
Recently we reported[1] that the rhodium(II)-acetate catalyzed C−H insertion in indoline diazoamides, such as **1** (eq 1), resulted in the preferential formation of tetrahydropyrrolo[1,2-*a*]indole derivatives, **2** and **3**, in high yields. This process represents a useful and mild method for the construction of the pyrrolo[1,2-*a*]indole ring system.[2] Herein we report the results from our investigation into the intramolecular metallocarbenoid C−H insertion reaction of indoline diazoamides, typified by **9** and **10**, that possess a CH_2X substituent (where X = "heteroatom group") at the C-2 position of the indoline nucleus.

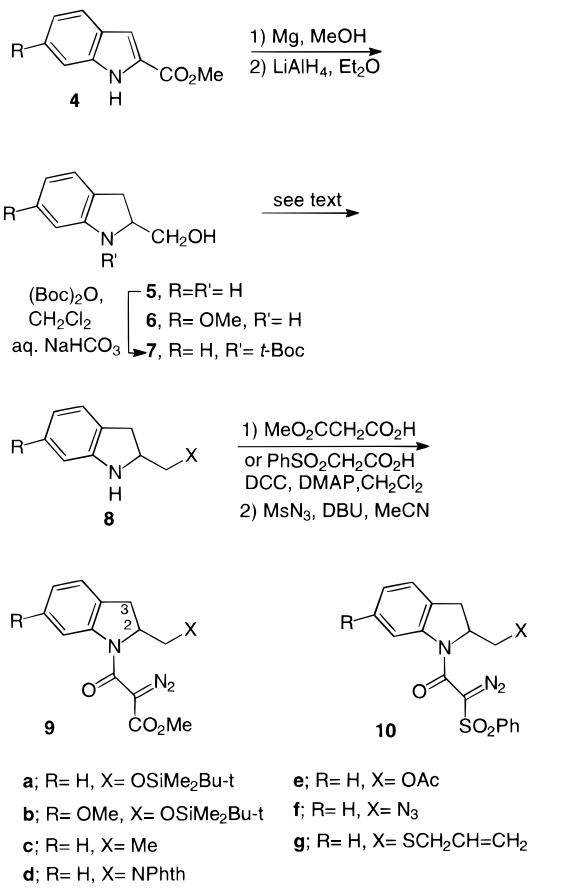


Results

The diazoamides **9** and **10** were prepared from the indoline alcohols **5**−**7**, which were readily obtained from the known[3] 2-indolecarboxylates **4** (R = H or OMe) (Scheme 1). Alcohols **5**−**7** were converted via standard functional group manipulations (supporting information) to yield the indoline derivatives **8a**−**g**. Acylation[1] of compounds **8** with either α-(carbomethoxy)acetic acid or α-(phenylsulfonyl)acetic acid gave the corresponding indoline amides, which were diazotized[1] (MsN_3, DBU) to yield the diazoamides **9** and **10**. We were unable to obtain **10d** in satisfactory yields because it was unstable and readily decomposed under the diazotization conditions. Therefore, the metal-catalyzed reaction of **10d** was not examined.

The metal-catalyzed reaction of diazoamides **9a**−**e** and **10 a**−**e** was conducted in refluxing dry CH_2Cl_2[4] and the results are summarized in Table 1. In general, three

Scheme 1



diastereomeric products, exo-trans (**EX-t**)-, exo-cis (**EX-c**)-, and endo-trans (**EN-t**)-**11** (Chart 1)[5] were obtained, which resulted from metallocarbenoid insertion into the methylene C−H of the CH_2X moiety. Aromatic substitution products were not detected in all the reactions studied, even in cases (entries 3−5, 10−12) where an electron-donating methoxy group was located *ortho* to the aromatic C−H bond. The formation of the diastereomer **EN-t-11** was unexpected when compared to the results obtained for **1** (eq 1).[1] The absence of the **EN-t**- and **EN-c**-type diastereomers in the reaction of **1** suggests that the transition states that led to these diastereomers were destabilized by an unfavorable *syn* Me/Me interaction (see **A**, R = Me, Chart 1) between the C-3 methyl group and the methyl moiety of the ethyl group. This destabilizing interaction is not present in the reactions of **9** and **10** (**A**, R = H) and, as a result, the **EN-t** and **EN-c** diasteromers were formed. The present results, and especially the data from the reaction of **9c** and **10c** (entries 6, 13), support this reasoning.

EN-t-11a, the diastereomers **11b** and **11h** were unstable and decomposed during chromatographic purification. Therefore, they were characterized as the pyrro-

(1) Wee, A. G. H.; Liu, B.-S.; Zhang, L. *J. Org. Chem.* **1992**, *57*, 4404.
(2) Some recent approaches, see for example: (a) Cotterill, A. S.; Hartopp, P.; Jones, G. B.; Moody, C. J.; Norton, C. L.; O'Sullivan, N. O.; Swann, E. *Tetrahedron* **1994**, *50*, 7657. (b) Ziegler, F. E.; Belema, M. *J. Org. Chem.* **1994**, *59*, 7962. (c) Michael, J. P.; Chang, S.-F.; Wilson, C. F. *Tetrahedron Lett.* **1993**, *34*, 8365. (d) Vedejs, E.; Piotrowski, D. W. *J. Org. Chem.* **1993**, *58*, 1341. (e) Shiue, J.-S.; Fang, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 1277. Review of earlier approaches see: Verboom, W.; Reinhoudt, D. N. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 199.
(3) Knittel, D. *Synthesis* **1985**, 186.
(4) We found that reaction temperature (rt vs reflux) had no influence on the diastereoselectivity and the chemoselectivity (C−H insertion versus O-interception) of the reaction.
(5) (a) Exo and endo refers to the orientation of X with respect to the convex side of tricyclic ring: exo = β-orietation and endo = α-orientation; cis and trans refer to the relative stereochemistry of X and R′ at C-1 and C-2 (pyrrolo[1,2-*a*]indole numbering), respectively. We thank a referee for bringing this designation to our attention. (b) The assignment of the relative stereochemistries at C-1, C-2, and C-9a was based on results obtained from difference NOE experiments performed on **EX-t**, **EX-c**, and **EN-t-12a,b**.

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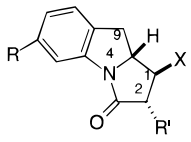
Table 1. Metal-Catalyzed Reaction of Indoline Diazoamides 9a-e and 10a-e in Refluxing CH_2Cl_2

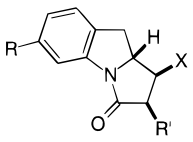
entry	diazoamide	catalyst[g]	diastereomers	interception[f]
1	**9a**	A	**EX-t/EX-c-11a**[a] (48%; 4.6:1[b]), **EN-t-11a** (38%)	n.d.[h]
2	**9a**	C	**EX-t/EX-c-11a**[a] (28%; 4.6:1[b]), **EN-t-11a** (4.1%)	**13a** (39%)
3	**9b**	A	**EX-t/EX-c-11b**[a] (47%; 3.7:1[b]), **EN-t-11b** (43%)	n.d.
4	**9b**	B	**EX-t/EX-c-11b**[a] (33%; 2.7:1[b]), **EN-t-11b** (18%)	n.d.
5	**9b**	C	**EX-t/EX-c-11b**[a] (34%; 2.7:1[b]), **EN-t-11b** (16.8%)	**13b** (10%)
6	**9c**	A	**EX-t/EX-c-11e**[a] (83%; 8.0:1[c]), **EN-t/EN-c-11e**[a] (12%; 7.3:1[c])	
7	**9d**	A	**EX-t-11g** (56%), **EX-c/EN-t-11g**[a] (25%; 1:10[c])	
8	**10a**	A	**EX-t/EX-c/EN-t-11c**[a] (67%; 9:1:2.5[c,d])	n.d.
9	**10a**	C	**EX-t/EX-c/EN-t-11c**[a] (80%; 5:1.5:4[c,d])	n.d.
10	**10b**	A	**EX-t/EX-c/EN-t-11d**[a] (84%; 8.7:1:1.4[c,d])	n.d.
11	**10b**	B	**EX-t/EX-c/EN-t-11d**[a] (60%; 19:1:1.4[c,d])	n.d.
12	**10b**	C	**EX-t/EX-c/EN-t-11d**[a] (76%; 1.5:0:1[c,d])	n.d.
13	**10c**	A	**EX-t/EX-c/EN-t-11f**[a] (77%; 9:1.1:1[c,d])	
14	**10e**	A	**EX-t/EX-c/EN-t-11h**[a] (72%)[e]	n.d.

[a] Obtained as an inseparable mixture of diastereomers. [b] Ratio is based on the integration of H-9a (major) and H-1 (minor). [c] Ratio is based on the integration of H-2. [d] Ratio is approximate due to overlap of the H-2/H-9a resonances; integration for H-2 is taken as $^1/_2$ total integration of the H-2/H-9a. [e] Ratio was not determined due to instability of product. [f] Heteroatom interception product. [g] A = $Rh_2(OAc)_4$, B = $Rh_2(Oct)_4$, C = $Cu(hfacac)_2$. [h] n.d. = Not detected.

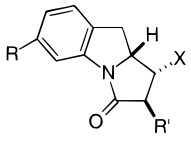
Chart 1



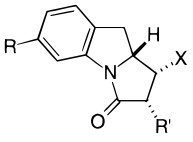
Exo-trans (**EX-t**)-**11**



Exo-cis (**EX-c**)-**11**

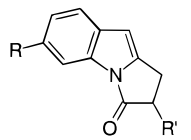


Endo-trans (**EN-t**)-**11**

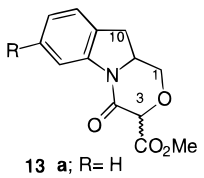


Endo-cis (**EN-c**)-**11**

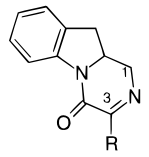
a; R= H, R'= CO_2Me, X= $OSiMe_2Bu$-t
b; R= OMe, R'= CO_2Me, X= $OSiMe_2Bu$-t
c; R= H, R'= SO_2Ph, X= $OSiMe_2Bu$-t
d; R= OMe, R'= SO_2Ph, X= $OSiMe_2Bu$-t
e; R= H, R'= CO_2Me, X= Me
f; R= H, R'= SO_2Ph, X= Me
g; R= H, R'= CO_2Me, X= NPhth
h; R= H, R'= SO_2Ph, X= OAc
i; R= H, R'= CO_2Me, X= $SCH_2CH{=}CH_2$
j; R= H, R'= SO_2Ph, X= $SCH_2CH{=}CH_2$



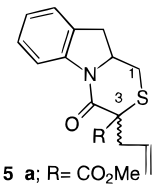
12 **a**; R=R'= H
b; R= OMe, R'= H
c; R=H, R'= SO_2Ph



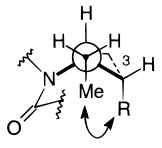
13 **a**; R= H
b; R= OMe



14 **a**; R= CO_2Me
b; R= SO_2Ph



15 **a**; R= CO_2Me
b; R= SO_2Ph



A R= Me
R= H

loindoles **12**; **EN-t-11a** and diastereomers **11b** were decarboxylated[6] to give **12a**[7] and **12b**, respectively. The diastereomers **11h** were treated with DBU in refluxing benzene to give the pyrroloindole **12c**.

The copper-catalyzed reaction of **9a,b** and **10a,b** proved interesting. It is well established that copper carbenoids are highly electrophilic,[8] but show diminished reactivity toward C−H insertion.[9,10] In addition, it was recently shown[11] that, unlike rhodium carbenoids, copper carbenoids react more efficiently with heteroatoms. The diazoamides **9a,b** furnished both C−H insertion and O-interception products (Table 1: entries 2,5); the latter products, **13a,b**, were generated with poor stereoselectivity. Thus **13a,b** were obtained as a 1:1 and 2:1 mixture of diastereomers, respectively. The data also indicated that **13a,b** were formed at the expense (in the yields) of the C−H insertion products, especially those of **EN-t-11a,b**. Unlike **9a,b**, the diazoamides **10a,b** gave only C−H insertion products (entries 9, 12); in the case of **10b**, the minor diastereomer, **EX-c-11d**, was not detected.

The interception of the Rh(II)-carbenoid by the X moiety was found to be the primary reaction pathway in the $Rh_2(OAc)_4$-catalyzed reaction of the diazoamides **9f,g** and **10f,g**. Thus, **9f** and **10f** gave only the interception product **14** (Chart 1). These results were surprising because the azide group was recently shown[12] to be effective in activating adjacent C−H bonds to metallocarbenoid insertion. To the best of our knowledge this is the first example of an interception of the Rh(II)-carbenoid by an azide group.[13] We found the yield of **14a** was dependent on the reaction temperature; in refluxing CH_2Cl_2, a yield of 55% was obtained (20% **9f** was also recovered), whereas in refluxing benzene a 76% yield was

(6) Krapcho, A. P. *Synthesis* **1982**, 893.
(7) (a) Cliff, G. R.; Jones, G.; Woollard, J. McK. **1973**, 2401. (b) Franck, R. W.; Auerbach, J. *J. Org. Chem.* **1971**, *36*, 31.
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(10) Recently, Lim and Sulikowski showed that copper carbenoids efficiently partake in C−H insertion reactions in α-(2-pyrrolidinophenyl)-α-diazoacetates wherein the carbenoid carbon and the C−H insertion site are held in close proximity. Sulikowski, G.; Lim, H.-J. *J. Org. Chem.* **1995**, *60*, 2326.
(11) (a) Clark, J. S.; Krowiak, S. A.; Street, L. J. *Tetrahedron Lett.* **1993**, *34*, 4385. (b) West, F. G.; Naidu, B. N.; Tester, R. W. *J. Org. Chem.* **1994**, *59*, 6892.
(12) (a) Wang, P.; Adams, J. *J. Am. Chem. Soc.* **1994**, *116*, 3296 and references cited.
(13) For an example of an interception of a carbene, generated under phase transfer reaction conditions, by an azide group see: Szonyi, F.; Cambon, A. *Tetrahedron Lett.* **1992**, *33*, 2339.

Table 2. NOE Results

	irradiate	observed NOE (%)	irradiate	observed NOE (%)
EX-t-11a	H-1	H-2 (3.2%), *trans*	H-1	H-9a (2.8%), *trans*
	H-2	H-9a (4.8%), *syn*		
EX-c-11a	H-1	H-2 (11%), *cis*		
EN-t-11a	H-1	H-9a (12%), *cis*	H-2	H-1 (3.8%), *trans*
EX-t-11c	H-9a	H-2 (4.4%), *syn*	H-1	H-2 (4%), *trans*
EX-c-11c	H-1	H-2 (16%), *cis*	H-1	H-9a (3.5%), *trans*

realized. On the other hand, the reaction of **10f** in refluxing CH_2Cl_2 resulted in complete conversion to the unstable **14b**. The structure of **14b** was assigned based on the ^{1}H NMR of the crude product, which showed a spectrum similar to that of **14a**. The characteristic features in the ^{1}H NMR are the double doublet centered at δ 3.74 due to H-1, the multiplet between δ 4.25 and 4.47 due to H-10a, and the double doublet centered at δ 4.67 attributed to H-1′.

The reaction of **9g** gave, in high yields (95%), a 12:1 ratio of the [2,3]-Wittig rearrangement[14] product **15a** and **11i** (relative stereochemistry at C-1/C-2 is unknown) as an inseparable mixture. The presence of **11i** was based on the observation of the characteristic H-5 doublet centered at δ 7.53. On the other hand, the reaction of **10g** resulted in a 3:1 ratio of **15b** to **EX-t-11j**, which was also obtained as an inseparable mixture. The presence of the latter compound was evidenced by the presence of the characteristic H-9a double triplet and H-2 doublet centered at δ 4.40 and 4.47, respectively.

In summary, the metal-catalyzed reaction of indoline diazoamides **9** and **10**, where X = OTBDMS, phthalimide (NPhth), and OAc, gave tetrahydropyrrolo[1,2-*a*]indole derivatives in good overall yields. However, O-interception products **13a,b** were also obtained in the copper-catalyzed reaction of **9a,b**. In diazoamides where X = N_3 and $SCH_2CH{=}CH_2$, the major products were derived from the interception of the metallocarbenoid by the X group.

Experimental Section

General. See reference 5 for general experimental procedures.

Metal-Catalyzed Reaction of Indoline Diazoamides. The appropriate indoline diazoamide **9** or **10** (1 mmol) was dissolved in dry CH_2Cl_2 (or PhH) under Ar. The metal catalyst (5 mol % $Rh_2(OAc)_4$ or $Rh_2(Oct)_4$ or 10 mol % $Cu(hfacac)_2$) was added, under Ar, to the solution, and the mixture was stirred either at rt or immediately immersed in an oil-bath set at 50 °C (90 °C when PhH was used). There was evolution of N_2 gas before the mixture started refluxing, and the color of the mixture changed from yellow to green (sometimes brown). The mixture was refluxed for 3−4 h and then cooled to rt, filtered, and evaporated. The residue was flash chromatographed to give **11**. Unless otherwise indicated, the ratio of diastereomeric mixtures is that observed for the $Rh_2(OAc)_4$-catalyzed reaction.

1-(*tert*-Butyldimethylsiloxy)-2-carbomethoxy-3-oxo-1,2,9,9a-tetrahydropyrrolo[1,2-*a*]indole (EX-t-/EX-c-11a). Off-white solid. Inseparable mixture, ratio 4.6:1. Yield: 48.6%. mp: 89−100 °C. IR υ_{max} (Nujol): 1756, 1737, 1712, 1605 cm^{-1}. ^{1}H NMR δ: 0.05, 0.10, and 0.12 (s, 6H); 0.90 (s, 9H); [2.94, J = 15.7, 10 Hz] and 3.03 (dd, J = 15.7, 9.8 Hz) (1H); 3.24 (dd, J = 15.7, 8.6 Hz) and [3.26, dd, J = 15.7, 8.6 Hz] (1H); [3.72, d, J = 8 Hz] and 3.83 (d, J = 9.5 Hz) (1H); [3.75] and 3.79 (s, 3H); 4.37 (dt, J = 9.3, 8.1 Hz) and [4.70−4.82, m] (1H); [4,54, t, J = 7.8 Hz] and 4.77 (dd, J = 10, 7.2 Hz) (1H); 6.98−7.09 (m, 1H); 7.13−7.25 (m, 2H); 7.49−7.60 (m, 1H). ^{13}C NMR δ: −4.78, [0.61], 17.83, 25.56, [30.00], 33.69, [52.21], 52.64, [60.49], 61.49, 66.96, [67.87], [75.85], 78.12, 115.42, 124.80, 125.39, 127.96, 133.23, [133.89], 138.80, 163.99, [167.06], 168.70. EIMS (m/z, rel intensity): 362 (M + 1, 100), 304 (M − t-Bu$^+$, 35), 230 (M + 1 − t-BuMe$_2$SiOH, 41). See Table 2 for NOE results. Anal. Calcd for $C_{19}H_{27}NO_4Si$: C, 63.13; H, 7.53; N, 3.88. Found: C, 63.41; H, 7.73; N, 3.91.

1-(*tert*-Butyldimethylsiloxy)-2-carbomethoxy-3-oxo-1,2,9,9a-tetrahydropyrrolo[1,2-*a*]indole (EN-t-11a). Pale yellow oil; yield 37.7%. IR υ_{max} (neat): 2953, 2856, 1737, 1707, 1606 cm^{-1}. ^{1}H NMR δ: 0.10 (s, 6H), 0.82 (s, 9H), 2.80 (dd, 1H, J = 14.5, 8.6 Hz), 3.38 (dd, 1H, J = 14.5, 9.6 Hz), 3.53 (s, 1H), 3.76 (s, 3H), 4.68 (d, 1H, J = 3.7 Hz), 4.96 (dt, 1H, J = 8.6, 3.7 Hz), 7.00 (dt, 1H, J = 7.7, 1.3 Hz), 7.10−7.25 (m, 2H), 7.58 (dd, 1H, J = 7.7, 1.3 Hz). ^{13}C NMR δ: −5.15, −4.95, 17.96, 25.50, 27.27, 52.66, 64.23, 67.14, 71.33, 114.86, 124.58, 125.21, 127.40, 134.21, 138.60, 164.81, 167.39. It was further characterized as **12a**. See Table 2 for NOE results.

1-(*tert*-Butyldimethylsiloxy)-2-carbomethoxy-6-methoxy-3-oxo-1,2,9,9a-tetrahydropyrrolo[1,2-*a*]indole (EX-t-/EX-c-11b). Pale yellow oil. Obtained as an inseparable mixture, ratio 3.7:1. Combined yield: 46.8%. IR υ_{max} (neat): 2954, 2856, 1746, 1713, 1616, 1593 cm^{-1}. ^{1}H NMR δ: 0.04 (s, 3H); 0.10 (s, 3H); 0.88 (s, 9H); [2.86, dd, J = 14.1, 10 Hz] and 2.94 (dd, J = 15.7, 9.6 Hz) (1H); [3.15, dd, J = 14.1, 8.7 Hz] and 3.17 (dd, J = 15.7, 8.8 Hz) (1H); [3.74] and 3.75 (s, 3H); [3.76] and 3.78 (s, 3H); [3.72, d, J = 7.9 Hz] and 3.82 (d, J = 9.4 Hz) (1H); 4.37 (dt, J = 9.8, 8.8, 7.6 Hz) and 4.69−4.80 (m) (1H); [4.52, t, J = 7.9 Hz] and 4.75 (dd, J = 9.4, 7.6 Hz) (1H), 6.57 (dd, 1H, J = 8.3, 2.5 Hz); [7.02, d, J = 8.3 Hz] and 7.03 (d, J = 8.3 Hz) (1H); 7.12 (d, J = 2.5 Hz) and [7.15, d, J = 2.5 Hz] (1H). ^{13}C NMR δ: −5.10, −4.29, 18.32, 26.07, [33.37], 33.48, [52.83], 53.15, 56.13, [61.08], 62.01, 68.26, [68.97], [76.29], 78.58, 101.81, 111.53, 125.27, [125.58], 126.19, 140.46, 160.32, [164.52], [167.74], 169.17. Due to the instability of this mixture, it was further characterized as compound **12b**.

1-(*tert*-Butyldimethylsiloxy)-2-carbomethoxy-6-methoxy-3-oxo-1,2,9,9a-tetrahydropyrrolo[1,2-*a*]indole (EN-t-11b). Pale yellow oil; yield 43%. IR υ_{max} (neat): 2954, 2856, 1747, 1711, 1661, 1601 cm^{-1}. ^{1}H NMR δ: 0.09 (s, 6H), 0.84 (s, 9H), 2.74 (dd, 1H, J = 15.1, 9.1 Hz), 3.31 (dd, 1H, J = 15.1, 9.9 Hz), 3.54 (s, 1H), 3.78 (s, 6H), 4.67 (d, 1H, J = 4.2 Hz), 4.97 (dt, 1H, J = 9.6, 4.2 Hz), 6.58 (dd, 1H, J = 8.2, 2.4 Hz), 7.05 (d, 1H, J = 8.2 Hz), 7.20 (d, 1H, J = 2.4 Hz). ^{13}C NMR δ: −5.11, −4.85, 18.07, 25.60, 26.64, 52.79, 55.54, 64.36, 68.06, 71.45, 100.89, 110.96, 125.56, 125.87, 139.60, 159.52, 164.88, 167.49. Due to the instability of this compound, it was further characterized as compound **12b**.

1-(*tert*-Butyldimethylsiloxy)-2-(phenylsulfonyl)-3-oxo-1,2,9,9a-tetrahydropyrrolo[1,2-*a*]indole (EX-t-/EX-c-/EN-t-11c). Off-white solid. Obtained as an inseparable mixture, ratio 9:1:2.5. Combined yield: 67%. IR υ_{max} (Nujol): 1712, 1687, 1604, 1323, 1155 cm^{-1}. ^{1}H NMR δ: [0.01], [0.14], [0.20], 0.26 and 0.30 (s, 6H); [0.85], 0.95 and [0.98] (s, 9H); 2.60−3.50 (m, 2H); [3.95, s], [4.12, d, J = 7.4 Hz] and 4.37 (d, J = 7.9 Hz), 4.32−4.44 (m), [4.77, t, J = 7.7 Hz], [4.87, t, J = 8.9 Hz], [4.97−5.10, m], 5.07 (dd, J = 7.7, 6.0 Hz) and [5.14, d, J = 4.5 Hz] (3H), 7.00−7.25 (m, 3H), 7.55−7.75 (m, 4H), 7.90−8.10 (m, 2H). See Table 2 for NOE results.

1-(*tert*-Butyldimethylsiloxy)-6-methoxy-2-(phenylsulfonyl)-3-oxo-1,2,9,9a-tetrahydropyrrolo[1,2-*a*]indole (EX-t-/EX-c-/EN-t-11d). White solid. Obtained as an inseparable mixture, ratio 6.7:1:1.3. Combined yield: 84%. Mp: 185−192 °C. IR υ_{max} (Nujol): 1698, 1614, 1588 cm^{-1}. ^{1}H NMR δ: [0.10, 0.12, 0.19], 0.22 and 0.30 (s, 6H); [0.85], 0.93 and [0.95] (s, 9H); 2.65−3.40 (m, 2H); 3.73, [3.75] and [3.78] (s, 3H); [3.96, s], [4.18, d, J = 7.7 Hz], 4.37 (d, J = 8.2 Hz), 4.32−4.45 (m), [4.76, t, J =8.2 Hz], [4.86, t, J = 8.5 Hz], [5.00−5.15, m] and 5.08 (dd, J = 7.7, 6.2 Hz) (3H); 6.55−6.64 (m, 1H); 7.00−7.18 (m, 2H); 7.50−

(14) (a) For a review: Padwa, A.; Hornbuckle, S. F. **1991**, *91*, 263. (b) A review of earlier work on [2,3]-Wittig rearrangement of sulfonium ylides see: Ando, W. *Acc. Chem. Res.* **1977**, *10*, 179.

7.71 (m, 3H); 7.93−8.07 (m, 2H). Anal. Calcd for $C_{24}H_{31}NO_5SSi$: C, 60.87; H, 6.60; N, 2.96. Found: C, 60.50; H, 6.64; N, 2.70.

1-Carbomethoxy-2-methyl-3-oxo-1,2,9,9a-tetrahydropyrrolo[1,2-*a*]indole (EX-t-/EXc-11e). Off-white solid. Obtained as a mixture, ratio 8:1. Combined yield: 83%. Mp: 111−115 °C. IR υ_{max} (Nujol): 1738, 1694, 1604 cm^{-1}. ^1H NMR δ: [1.19] and 1.25 (d, 3H, J = 7.4 Hz); [2.57−2.92, m] and 2.95 (dd, J = 15.4, 9.7 Hz) (2H); [3.18] and 3.21 (dd, 1H, J = 15.4, 8.7 Hz); 3.52 (J = 11.4 Hz) and [3.63, J = 8.5 Hz] (d, 1H); [3.77] and 3.81 (s, 3H); [4.12, J = 7.2 Hz] and 4.18 (J = 8.7 Hz) ("q"); 6.98−7.09 (m, 1H); 7.14−7.27 (m, 2H); 7.52−7.62 (m, 1H). ^{13}C NMR δ: [12.73], 15.63, 33.79, [41.69], 42.87, [52.10], 52.44, [59.23], 60.09, 66.65, [67.64], 114.78, [114.94], 124.44, [124.52], 125.30, 127.64, 133.61, [134.35], 138.90, 166.15, 168.84. EIMS (m/z, rel intensity): 246 (M^+ + 1, 27), 245 (M^+, 100), 186 (M − CO_2Me, 43). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.54; H, 6.17; N, 5.71. Found: C, 68.81; H, 6.17; N, 5.47.

1-Carbomethoxy-2-methyl-3-oxo-1,2,9,9a-tetrahydropyrrolo[1,2-*a*]indole (EN-t-/EN-c-11e). Pale yellow oil. Obtained as a mixture, ratio 7.3:1. Combined yield: 12%. IR υ_{max} (film): 1732, 1698, 1604 cm^{-1}. ^1H NMR δ: [1.05] and 1.15 (d, 3H, J = 7.3 Hz); 2.80−3.22 (m, 3H); 3.32 (s) and [4.02, d, J = 6.7 Hz] (1H); [3.78] and 3.81 (s, 3H); [4.74] and 5.04 (J = 9.2, 5.9 Hz); 6.99−7.10 (m, 1H); 7.15−7.30 (m, 2H); 7.58−7.69 (m, 1H). ^{13}C NMR δ: [11.32], 15.55, 28.58, [28.70], 35.38, [35.64], 52.73, [57.23], 62.47, [63.32], 64.59, [114.59], 114.90, [124.34], 124.67, 125.44, 127.72, 134.20, 138.43, 165.21, 169.27. EIMS (m/z, rel intensity): 246 (M^+ + 1, 22), 245 (M^+, 100), 186 (M − CO_2Me, 45). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.54; H, 6.17; N, 5.71. Found: C, 68.71; H, 6.17; N, 5.39.

1-Methyl-3-oxo-2-(phenylsulfonyl)-1,2,9,9a-tetrahydropyrrolo[1,2-*a*]indole (EX-t-/EX-c-/EN-t-11f). Crystalline solid. Obtained as a mixture, ratio 8.9:1.1:1. Combined yield: 77%. Mp: 228−231 °C. IR υ_{max} (Nujol): 1694, 1604 cm^{-1}. ^1H NMR δ: [1.20], 1.51 and [1.70] (d, 1H, J = 7 Hz); 2.83−3.60 (m, 3H); [3.73, s], [4.01, d, J = 7.7 Hz] and 4.08 (d, J = 10.2 Hz) (1H); 4.12 ("q", J = 8.5 Hz), [4.85, "q", J = 9 Hz] and [5.12, br t, J = 7.7 Hz] (1H); 6.90−7.25 (m, 3H); 7.32−7.80 (m, 4H); 7.85−8.10 (m, 2H). Anal. Calcd for $C_{18}H_{17}NO_3S$: C, 66.04; H, 5.23; N, 4.28. Found: C, 66.24; H, 5.26; N, 4.31.

2-Carbomethoxy-3-oxo-1-phthalimido-1,2,9,9a-tetrahydropyrrolo[1,2-*a*]indole (EX-t-11g). Off-white solid; yield 55.7%. Mp: 196.3−197.6 °C. IR υ_{max} (Nujol): 1773, 1745, 1715, 1604 cm^{-1}. ^1H NMR δ: 3.19 (d, 2H, J = 8.9 Hz), 3.77 (s, 3H), 5.01 (d, 1H, J = 11.1 Hz), 5.03 (q, 1H, J = 8.9 Hz), 5.39 (dd, 1H, J = 11.1, 8.9 Hz), 7.07 (dt, 1H, J = 7.8, 1.1 Hz), 7.19 (br d, 1H, J = 7.8 Hz), 7.24 (br t, 1H, J = 7.8 Hz), 7.59 (br d, 1H, J = 7.8 Hz), 7.72−7.43 (m, 4H). ^{13}C NMR δ: 33.73, 52.83, 53.56, 54.86, 61.43, 115.22, 123.62, 124.94, 125.33, 127.84, 131.30, 132.89, 134.47, 138.64, 163.39, 167.44, 167.52. EIMS (m/z, rel intensity): 376 (M^+, 19), 229 (M − HNPhth, 93). Anal. Calcd for $C_{21}H_{16}N_2O_5$: C, 67.00; H, 4.29; N, 7.45. Found: C, 66.72; H, 4.09; N, 7.28.

2-Carbomethoxy-3-oxo-1-phthalimido-1,2,9,9a-tetrahydropyrrolo[1,2-*a*]indole (EX-c-/EN-t-11g). Crystalline product; obtained as an inseparable mixture, ratio 1:11. Combined yield: 25.3%. Mp: 188.5−190.0 °C. IR υ_{max} (Nujol): 1770, 1727, 1714, 1607 cm^{-1}. ^1H NMR δ: 2.76 (dd, 1H, J = 16.1, 10.1 Hz); 2.99 (dd, 1H, J = 16.1, 10.1Hz); [3.59] and 3.82 (s, 3H); 3.85 (s) and [4.24, d, J = 7.3 Hz] (1H); [5.07, J = 9.7, 6 Hz] and 5.26 (J = 9.7, 7.3 Hz) (dt, 1H); 5.46 (dd, J = 7, 1.7 Hz) and [5.48, t, J = 7 Hz] (1H); 7.03 (dt, 1H, J = 7.2 Hz); 7.15 (br d, 1H, J = 7.2 Hz); 7.23 (br t, 1H, J = 7.2 Hz); 7.56 (br d, 1H, J = 7.2 Hz); 7.72−7.86 (m, 4H). Anal. Calcd for $C_{21}H_{16}N_2O_5.{}^1/_4H_2O$: C, 66.21; H, 4.36; N, 7.36. Found: C, 66.39; H, 4.03; N, 7.15.

1-Acetoxy-2-(phenylsulfonyl)-3-oxo-1,2,9,9a-tetrahydropyrrolo[1,2-*a*]indole (EX-t-/EX-c-/EN-t-11h). Unstable, pale yellow solid; yield 72%. ^1H NMR δ ($CDCl_3$/MeCN-d_3): [2.02], [2.06] and 2.14 (s, 3H); 2.90−3.70 (m, 2H); [4.30, s], [4.50, d, J = 6.4 Hz], 4.75 (dt, J = 10.2, 3.8 Hz), 4.85 (d, J = 5.4 Hz), [5.14, dt, J = 10.2, 5.1 Hz], [5.57, t, J = 8.7 Hz], [5.68, dd, J = 8.7, 7.2 Hz], [5.90, d, J = 5.1 Hz] and 6.18 (t, J = 5.1 Hz) (3H); 7.00−7.30 (m, 3H); 7.50−7.80 (m, 4H); 7.90−8.20 (m, 2H). This mixture was unstable and was characterized as compound **12c**.

3-Carbomethoxy-4-oxo-3,4,10,10a-tetrahydro-1*H*-[1,4]oxazino[4,3-*a*]indole (13a). Crystalline, colorless solid. Obtained as an inseparable, 1:1 mixture of diastereomers; yield 39%. IR υ_{max} (film): 1749, 1666, 1601 cm^{-1}. ^1H NMR δ: [2.89] and 2.94 (dd, 1H, J = 12.3, 4.1 Hz); 3.13 and [3.19] (dd, 1H, J = 12.3, 8.2 Hz); [3.82] and 3.87 (s, 3H); 4.27−4.73 (m, 3H, H-1); [4.84] and 4.93 (s, 1H); 7.05−7.15 (m, 1H); 7.19−7.30 (m, 2H); 7.95−8.08 (m, 1H). Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.66. Found: C, 63.06; H, 5.12; N, 5.43.

3-Carbomethoxy-6-methoxy-4-oxo-3,4,10,10a-tetrahydro-1*H*-[1,4]oxazino[4,3-*a*]indole (13b). Crystalline, orange solid. Obtained as an inseparable, 2:1 mixture of diastereomers; yield 10%. Mp: 138−143 °C. IR υ_{max} (film): 1743, 1667, 1612, 1596, 1532 cm^{-1}. ^1H NMR δ: [2.73] and 2.80 (dd, 1H, J = 11, 4 Hz); 3.00 and [3.08] (t, 1H, J = 8.8 Hz); 3.75, 3.77 and 3.82 (s, 6H); 4.19−4.69 (m, 3H); [4.79] and 4.87 (s, 1H); 6.61 (dd, 1H, J = 8.2, 2.1 Hz); 7.06 (d, 1H, J = 8.2 Hz); [7.61] and 7.64 (d, 1H, J =2.1 Hz). Anal. Calcd for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.52; H, 5.46; N, 4.99.

3-Carbomethoxy-1,4,10,10a-tetrahydro-4-oxopyrazino-[1,2-*a*]indole (14a). Bright yellow solid; yield 55% (CH_2Cl_2); 76% (PhH). Mp: 119.2−120.4 °C. IR υ_{max} (Nujol): 1732, 1666, 1633, 1599 cm^{-1}. ^1H NMR, δ: 2.97 (dd, 1H, J = 16, 10.3), 3.37 (dd, 1H, J = 16, 8.7 Hz), 3.65 (dd, 1H, J = 17.1, 13.2 Hz), 3.96 (s, 3H), 4.34 (d sept, 1H, J = 13.2, 10.3, 8.7, 4.2 Hz), 4.53 (dd, 1H, J = 17.1, 4.2 Hz), 7.14 (dt, 1H, J = 7.5, 1.4 Hz), 7.23−7.33 (m, 2H), 8.08 (br d, 1H, J = 7.5 Hz). ^{13}C NMR δ: 33.13, 52.98, 53.63, 55.37, 116.52, 124.88, 125.43, 128.10, 129.37, 140.37, 150.78, 157.55, 163.34. Anal. Calcd for $C_{13}H_{12}N_2O_3$: C, 63.91; H, 4.95; N, 11.47. Found: C, 63.98; H, 4.74; N, 11.47.

4-Oxo-3-(phenylsulfonyl)-1,4,10,10a-tetrahydropyrazino-[1,2-*a*]indole (14b). This compound was the only product formed as judged by TLC, but is highly unstable; attempted chromatographic purification resulted in complete decomposition. The crude product on storage slowly decomposes. The data obtained is for the unpurified material. IR υ_{max} (Nujol): 1674, 1633, 1599, 1583 cm^{-1}. ^1H NMR δ: 2.92 (dd, 1H, J = 15.4, 10.8 Hz), 3.35 (dd, 1H, J = 15.7, 7.7 Hz), 3.74 (dd, 1H, J = 16.9, 13.7 Hz), 4.25−4.47 (m, 1H), 4.67 (dd, 1H, J = 16.9, 4.3 Hz), 7.00−7.32 (m, 3H), 7.45−7.86 (m, 3H), 8.00−8.20 (m, 3H).

3-Allyl-3-carbomethoxy-4-oxo-3,4,10,10a-tetrahydro-1*H*-[1,4]thiazino[4,3-*a*]indole (15a) and 11i. Pale yellow oil; yield 95%. Obtained as an inseparable mixture consisting of a diastereomeric mixture of **15a** and **11i**. IR υ_{max} (neat): 3077, 2952, 2847, 1741, 1650, 1599 cm^{-1}. ^1H NMR: For **15a**: δ: 2.64−3.57 (m, 6H), 3.75 (s, 3H), 4.33−4.52 and 4.52−4.71 (m, 1H), 5.06−5.10 (m, 2H), 5.75−6.01 (m, 1H), 7.00−7.30 (m, 3H), 8.14 and 8.22 (d, 1H, J = 8 Hz). Discernible signal for **11i**: δ 7.53 (d, J = 8 Hz). Anal. Calcd for $C_{16}H_{17}NO_3S$: C, 63.35; H, 5.65; N, 4.62. Found: C, 63.07; H, 5.65; N, 4.68.

3-Allyl-4-oxo-3-(phenylsulfonyl)-3,4,10,10a-tetrahydro-1*H*-[1,4]thiazino[4,3-*a*]indole (15b) and EX-t-11j. Pale yellow solid. Obtained as an inseparable mixture. Yield: 92%. IR υ_{max} (Nujol): 1710, 1651, 1600 cm^{-1}. ^1H NMR: For **15b**: δ: 2.55 (dd, J =12.8, 7.7 Hz), 2.80−3.45 (m), 3.65−4.05 (m), 4.61 (d quint, J = 10.2, 7.7, 2.5 Hz), 4.95 (dq, J = 8.9, 3.8 Hz) 5.10−5.45 (m) and 5.60−6.00 (m) (10H), 7.00−7.30 (m, 3H), 7.45−8.12 (m, 6H). Discernible resonance for **EX-t-11j**: δ 4.40 (dt, J = 10.2, 8.2 Hz) and 4.47 (d, J = 8.9 Hz). Anal. Calcd for $C_{20}H_{19}NO_3S_2$: C, 62.31; H, 4.97; N, 3.63. Found: C, 62.41; H, 5.00; N, 3.55.

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Supporting Information Available: Spectroscopic and analytical data for diazoamides **9a**−**g** and **10a**−**g**, **12a**−**c**, ^1H NMR spectra of **14b**, table listing multiplicity and δ for H-1 and H-2 in **11a**−**d**, and a chart illustrating the synthesis of **8a**−**g** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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