6.10 (AB q, J = 1.2 Hz, 2 H), 4.90 (d, J = 11.7 Hz, 1 H), 3.96 (s, 3 H), 3.95 (s, 3 H), 3.55 (m, 1 H), 3.31 (dd, J = 15.9, 4.3 Hz, 1 H), 3.17 (s, 3 H), 2.64 (dd, J = 15.9, 13.9 Hz, 1 H); MS m/e (relative intensity) 381 (54, M^+), 353 (7), 352 (11), 350 (7), 232 (12), 191 (18), 165 (100), 147 (16). This compound was identical (TLC) with an authentic sample.[11]

12-Methyl-[1,3]benzodioxolo[5,6-*c*]phenanthridin-13(12*H*)-one (12). The ketone **10** (400 mg, 1.25 mmol) was dissolved in 100 mL of 2-propanol by warming on a steam bath, and the solution was treated with 200 mg of $NaBH_4$ at room temperature. After 3 h, the solvent was removed in vacuo and the residue was cautiously acidified with concentrated HCl and extracted with $CHCl_3$. The combined $CHCl_3$ extracts were washed successively with 2% sodium hydroxide solution, water, and brine, dried (Na_2SO_4), and evaporated. The crude mixture of alcohols thus obtained was dissolved in 100 mL of acetic acid and stirred at reflux with 200 mg of 10% Pd–C overnight. After cooling to room temperature, the reaction mixture was filtered through Celite, and the residue was washed with $CHCl_3$. The combined filtrate and washings were concentrated in vacuo, and the residue was treated with 2% sodium hydroxide solution and extracted thoroughly with $CHCl_3$. The combined $CHCl_3$ extracts were washed with brine, dried (Na_2SO_4), and evaporated, and the residue was chromatographed on silica gel ($CHCl_3$) to give 179 mg (47%) of **12**: mp 235–237 °C; NMR ($CDCl_3$) δ 8.54 (d, J = 7.9 Hz, 1 H), 8.25 (d, J = 7.9 Hz, 1 H), 8.10 (d, J = 8.8 Hz, 1 H), 7.76 (t, J = 8.3 Hz, 1 H), 7.62 (s, 1 H), 7.60–7.55 (m, 2 H), 7.17 (s, 1 H), 6.10 (s, 2 H), 3.97 (s, 3 H); MS m/e (relative intensity) 303 (100, M^+), 302 (82), 274 (24), 245 (18), 216 (17). Exact mass calcd for $C_{19}H_{13}NO_3$: 303.0895. Found: 303.0892. Anal. Calcd for $C_{19}H_{13}NO_3$: C, 75.24; H, 4.32; N, 4.62. Found: C, 75.29; H, 4.36; N, 4.57.

Also isolated was 58 mg (15%) of the tetrahydro compound **14**: mp 192–193 °C; NMR ($CDCl_3$) δ 8.10 (dd, J = 7.7, 1.4 Hz, 1 H), 7.48 (dt, J = 7.5, 1.5 Hz, 1 H), 7.39 (t, J = 7.5, 1.3 Hz, 1 H), 7.30 (d, J = 7.5 Hz, 1 H), 6.72 (s, 1 H), 6.66 (s, 1 H), 5.96 (AB q, J = 1.4 Hz, 2 H), 4.72 (d, J = 11.5 Hz, 1 H), 3.13 (dt, J 12.2, 3.1 Hz, 1 H), 3.11 (s, 3 H), 3.01–2.77 (m, 2 H), 2.55–2.47 (m, 1 H), 1.66 (dq, J = 11.9, 4.7 Hz, 1 H); MS m/e (relative intensity) 307 (76, M^+), 279 (100), 278 (59), 189 (19), 172 (21). Exact mass calcd for $C_{19}H_{17}NO_3$: 307.1208. Found: 307.1207. Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.35; H, 5.53; N, 4.51.

Oxynitidine (2,3-Dimethoxy-12-methyl-[1,3]benzodioxolo[5,6-*c*]phenanthridin-13(12*H*)-one) (13). The ketone **11** (200 mg) was reduced and dehydrogenated as described for **10** to give a mixture that was chromatographed on silica gel (3% MeOH–CH_2Cl_2) to give 74 mg (49%) of oxynitidine **13**: mp 280–283 °C (lit.[5f] mp 284–285 °C); NMR ($CDCl_3$) δ 8.00 (d, J = 8.7 Hz, 1 H), 7.94 (s, 1 H), 7.65 (s, 1 H), 7.60 (s, 1 H), 7.57 (d, J = 8.7 Hz, 1 H), 7.19 (s, 1 H), 6.11 (s, 2 H), 4.11 (s, 3 H), 4.06 (s, 3 H), 3.99 (s, 3 H); MS m/e (relative intensity) 363 (100, M^+).

Also isolated was 30 mg (15%) of the tetrahydro compound **15**: mp 225–227 °C; NMR ($CDCl_3$) δ 7.64 (s, 1 H), 6.77 (s, 1 H), 6.74 (s, 1 H), 6.66 (s, 1 H), 5.96 (AB q, J = 1.9 Hz, 2 H), 4.70 (d, J = 11.4 Hz, 1 H), 3.96 (s, 3 H), 3.95 (s, 3 H), 3.11 (s, 3 H), 3.10–2.78 (m, 3 H), 3.50 (m, 1 H), 2.70 (m, 1 H); MS m/e (relative intensity) 367 (100, M^+), 252 (6), 339 (93), 338 (36), 324 (15), 232 (31), 165 (92). Exact mass calcd for $C_{21}H_{21}NO_5$: 367.1420. Found: 367.1422.

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Registry No. **1**, 2728-04-3; **2**, 113975-92-1; **2** (acid), 20736-28-1; **2** (acid chloride), 91940-89-5; **3**, 113975-93-2; **4**, 113975-94-3; **5**, 113975-95-4; **6**, 113975-96-5; **7**, 113975-97-6; **8**, 113975-98-7; **9**, 64036-04-0; **10**, 113975-99-8; **11**, 64036-03-9; **12**, 113976-00-4; **13**, 548-31-2; **14**, 113976-01-5; **15**, 56221-65-9; **17**, 87922-31-4; $BrCH_2CH(OMe)_2$, 7252-83-7; 6-bromoveratraldehyde ethylene acetal, 103477-58-3; 6-methylveratraldehyde ethylene acetal, 113976-02-6; 6-methylveratraldehyde, 7721-62-2; ethylene oxide, 75-21-8.

Highly Reactive Copper- and Nickel-Mediated Coupling of Aroyl Chlorides

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Reductive coupling of benzoyl chlorides using sodium amalgam,[1-4] lithium amalgam,[5] tetracarbonylnickel,[6] pentacarbonyliron,[7] hexaalkylditin,[8] 1,2:5,6-dibenzocyclooctatetraene dianion,[9] and mercury cathode[10,11] to give a mixture of *cis*- and *trans*-α,α'-stilbenediol dibenzoates has been previously reported. The mechanism proposed involves reduction of the acid chloride to generate the acyl radical.[7,12] Recently, we have found similar results using highly reactive zerovalent copper and nickel.

We previously reported the direct oxidative addition of highly reactive zerovalent copper to organic halides.[13-17] The exceptionally high reactivity of this copper suggests that it may also be a very good electron donor to carry out the reductive coupling of acid chlorides. In this paper, we report the results of this study.

Table I summarizes some reactions of aroyl chlorides with highly reactive zerovalent copper.[18] The yields are superior to those reported earlier using sodium amalgam (0–10%),[1-4] tetracarbonylnickel (0–30%),[6] pentacarbonyliron (52–56%),[7] hexaalkylditin (20–64%),[8] and 1,2:5,6-dibenzocyclooctatetraene dianion (51%).[9] The reaction conditions are extremely mild (−78 °C) and the stereoselectivity (predominantly *cis* isomer)[12] is considerably higher than reported previously.[1-11] It is also noteworthy that the effects of solvent on the reductive

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(18) Spectral data are as follows. *cis-p,p'*-Dichlorostilbene-α,α'-diol bis(*p*-chlorobenzoate): mp 167–168 °C; IR (KBr) 1740, 1590, 1485, 1400, 1265, 1240, 1170, 1080, 1045, 1005, 845, 820, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (d, 4 H), 7.32 (d, 4 H), 7.36 (d, 4 H), 7.94 (d, 4 H). *cis*-α,α'-Stilbenediol bis(*p*-chlorobenzoate): mp 159–161 °C; IR (KBr) 1740, 1590, 1485, 1440, 1400, 1250, 1235, 1125, 1105, 1080, 1005, 840, 760, 745, 690, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26 (m, 6 H), 7.35 (d, 4 H), 7.39 (d, 4 H), 7.97 (d, 4 H); ^{13}C NMR ($CDCl_3$) δ 127.57, 128.44, 128.96, 129.09 (2 C), 131.43, 133.03, 139.06, 140.27, 163.30; MS (EI) m/e (relative intensity) 488 (M^+, 1.1), 139 (100.0). Calcd for $C_{28}H_{18}O_4Cl_2$ (M^+) m/e 488.0582; found m/e 488.0592. *trans*-α,α'-Stilbenediol bis(*p*-chlorobenzoate): mp 231–232 °C; MS (EI) m/e (relative intensity) 488 (M^+, 0.6), 139 (100.0). *p,p'*-Dichlorobenzil: mp 194–196 °C (lit.[30] mp 195–197 °C); IR (KBr) 1660, 1585, 1570, 1485, 1400, 1315, 1205, 1170, 1090, 1075, 1005, 875, 830, 760, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50 (d, 4 H), 7.92 (d, 4 H).

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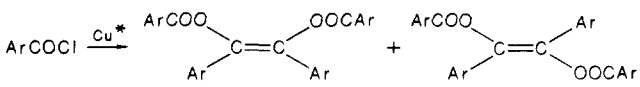
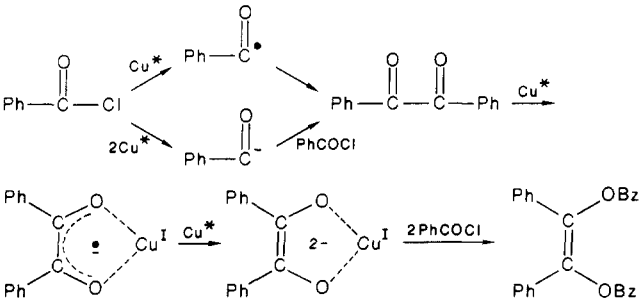
Table I. Reactions of Aroyl Chlorides with Activated Copper



entry	reactant (equiv)[a]	conditions	% yield	cis/trans
1	PhCOCl (0.5)	THF, −78 °C	82	93:7[b,c]
2	PhCOCl (0.5)	THF, 0 °C	80	93:7[b,c]
3	PhCOCl (1.0)	THF, 0 °C	79	93:7[b,c]
4	PhCOCl (1.0)	$PhCH_3$, −78 °C	81	95:5[b,c]
5	p-ClC_6H_4COCl (1.0)	THF, −78 → 0 °C	82	90:10[b,c]
6	2-furoyl chloride (0.85)	THF, 0 °C	*d*	~1:1[c]

[a] The amount of acid chlorides used relative to that of the activated copper. [b] Pure cis isomer was obtained by recrystallization, but pure trans isomer could not be isolated. [c] Ratio of cis and trans isomers was determined by NMR spectroscopy. [d] Reaction gave the coupled products in moderate yield; however, the products were readily decomposed.

Scheme I



coupling of benzoyl chlorides are slight. Remarkably, the activated copper reacts with the benzoyl chlorides at temperature as low as −78 °C. Aliphatic acid chlorides have also been tried; however, the reaction yielded a complex mixture and the products were not fully characterized.

In support of our proposed mechanism (Scheme I), stilbenediol radical anion (one of the suggested intermediates) was trapped by chlorotrimethylsilane to form presumably the trimethylsilyl enol ether, which spontaneously decomposed to give benzoin during the aqueous workup. As shown in eq 1 and 2, the reactions give high

$$PhCOCl \xrightarrow[TMSCl]{Cu^*,\ THF} PhCOCH(OH)Ph\ (66\%) \quad (1)$$

$$ArCOCl \xrightarrow[TMSCl]{Cu^*,\ THF} ArCOCH(OH)Ar \xrightarrow{air} ArCOCOAr \quad (2)$$

$$Ar = p\text{-}ClC_6H_4$$

yields of benzoin; however, p,p'-dichlorobenzoin was readily oxidized in air to produce p,p'-dichlorobenzil.[18] Acyloin reactions[19] and α-diketone synthesis[20,21] for carboxylic acid chlorides were not well developed. The coupling of acid chlorides into α-hydroxy ketones promoted by activated copper in the presence of chlorotrimethylsilane could be developed as a useful synthetic method. The reduction step converting benzil to stilbenediol radical anion is also supported by reacting benzil with the activated copper (eq 3). On treatment with highly reactive

$$1.0PhCOCOPh \xrightarrow[(b)\ ArCOCl]{(a)\ 1.0Cu^*} Ph(ArCOO)C{=}C(OOCAr)Ph\ (49\%\ \text{isolated}) + PhCOCOPh\ (50\%\ GC) \quad (3)$$

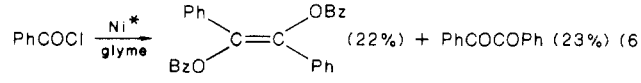
$$Ar = p\text{-}ClC_6H_4$$

copper in THF, benzil was presumably transformed to the stilbenediol radical anion, which is trapped by benzoyl chloride to form the stilbenediol dibenzoate (eq 3). The reaction of equal molar quantities of benzil and activated copper, followed by the addition of an excess p-chlorobenzoyl chloride, yielded approximately 50% (GC) of unreacted benzil and a 49% isolated yield of a mixture of *cis*- and *trans*-α,α'-stilbenediol bis(p-chlorobenzoate)[18] in a 7:1 cis:trans ratio. This observation suggests that a copper(I) species is involved in these reactions and not a copper(II) species. Reaction of an equal molar quantity of benzil and activated copper in THF afforded benzoin and unreacted benzil in a 1:1.2 ratio, again suggesting a copper(I) species is involved in these reactions (eq 4). It is of interest to note that the stilbenediol radical anion can also undergo an alkylation reaction with iodomethane to produce α-methylbenzoin in excellent yield (eq 5).

$$1.0PhCOCOPh \xrightarrow[(b)\ H^+]{(a)\ 1.0Cu^*} PhCOCH(OH)Ph\ (45\%) + PhCOCOPh\ (55\%) \quad (4)$$

$$PhCOCOPh \xrightarrow[(b)\ CH_3I]{(a)\ Cu^*} PhCOCMe(OH)Ph\ (88\%) \quad (5)$$

The activated nickel powder[22-25] generated from nickel(II) iodide (1.0 equiv), lithium (2.2 equiv), and naphthalene (0.1 equiv) reacts with benzoyl chloride in glyme at room temperature to give benzil and *trans*-α,α'-stilbenediol dibenzoate in a 1:1 ratio (eq 6). It is interesting



that both activated copper and activated nickel give similar results, however, with the opposite stereoselectivity. The activated copper gave predominantly the cis isomer,[12] whereas the activated nickel produced predominantly the trans isomer.[26]

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. IR spectra were taken on a Perkin-Elmer 283 spectrophotometer neat between NaCl plates or as KBr disks. ^1H NMR spectra were recorded on a Nicolet NT-360 (360 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Varian VXR-200 (50 MHz) spectrometer. All chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. High-resolution mass spectra were performed by the Midwest Center for Mass Spectrometry at the University of Nebraska—Lincoln using a Kratos MS-80 mass spectrometer. Gas chromatography analysis was done on a Hewlett-Packard 5890A chromatograph using a stainless steel column packed with OV-17 (3%) on Chromosorb G.

All manipulations were carried out on a dual-manifold vacuum/argon system. The Linde prepurified grade argon was further purified through a 150 °C catalyst column (BASF R3-11), a phosphorus pentoxide column, and a column of granular potassium hydroxide. Tetrahydrofuran and 1,2-dimethoxyethane were

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freshly distilled under argon from sodium/potassium alloy. Anhydrous copper(I) iodide and nickel(II) iodide were purchased from Cerac, Inc. Lithium and naphthalene were weighed out and charged into reaction flasks under argon in a Vacuum Atmospheres Co. drybox. Other commercially available reagents were used as received.

Typical Preparation of Activated Copper. A 50-mL two-necked round-bottomed flask was equipped with a rubber septum, a condenser topped with an argon inlet, and a stir bar. The flask was charged with naphthalene (8.7 mmol) and freshly cut lithium (7.2 mmol) in the drybox and was then connected to the manifold system. The freshly distilled THF (5 mL) was added via syringe, and the mixture was stirred at room temperature for 2 h. A solution of $CuIP(n\text{-}Bu)_3$ (6.7 mmol) prepared in situ from CuI (6.7 mmol) and $P(n\text{-}Bu)_3$ (7.2 mmol) in THF (10 mL) was transferred into the preformed lithium naphthalide via cannula at 0 °C and stirred at 0 °C for 0.5 h.

Reductive Coupling of Benzoyl Chloride Using Activated Copper. Benzoyl chloride (460 mg, 3.27 mmol) was added to the freshly prepared activated copper (6.7 mmol) via syringe with stirring at −78 °C in a dry ice–acetone bath. The reaction mixture was stirred at −78 °C for 10 min and then quenched with 3% aqueous HCl solution.[26] The reaction solution was extracted twice with CH_2Cl_2. The combined organic layers were washed with H_2O, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting mixture was chromatographed on silica gel to give stilbenediol dibenzoate (280 mg, 81.5%) as a white solid. Pure *cis*-α,α'-stilbenediol dibenzoate can be obtained by continuous recrystallization from a pentane–EtOAc solution: mp 157.5–158.5 °C (lit.[4] mp 159 °C); IR (KBr) 1735, 1595, 1450, 1270, 1240, 1090, 1070, 1050, 1020, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26 (m, 6 H), 7.36 (t, 4 H), 7.43 (d, 4 H), 7.51 (t, 2 H), 8.09 (d, 4 H); ^{13}C NMR ($CDCl_3$) δ 128.33, 128.42, 128.90, 129.09, 129.21, 130.07, 133.34, 133.40, 139.07, 164.20.

Reductive Coupling of Benzoyl Chloride Using Activated Copper in the Presence of Trimethylchlorosilane (TMSCl). To freshly prepared activated copper (15.86 mmol) was added TMSCl (6.3 mL, 49.64 mmol) via syringe at −78 °C. Benzoyl chloride (1.12 g, 7.97 mmol) in THF (10 mL) was added dropwise via syringe over a 20-min period. The reaction mixture was stirred at −78 °C for 0.5 h. The dry ice–acetone bath was then replaced with an ice–H_2O bath. After stirring at 0 °C for 3 h, the reaction mixture was allowed to warm to room temperature. The reaction was quenched with H_2O (30 mL), and the resulting mixture was extracted with ether. The combined organic layers were washed with H_2O, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting mixture was flash chromatographed on silica gel to give benzoin (561 mg, 66.3%) as a white powder: mp 134–135 °C (lit.[28] mp 134–135.5 °C); IR (KBr) 3200–3500 (br), 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.57 (d, J = 6.0 Hz, 1 H), 5.96 (d, J = 6.0 Hz, 1 H), 7.27–7.34 (m, 5 H), 7.40 (t, 2 H), 7.53 (t, 1 H), 7.92 (d, 2 H).

Reductive Alkylation of Benzil Using Activated Copper. To freshly prepared activated copper (15.71 mmol), benzil (1.642 g, 7.81 mmol) in THF (10 mL) was added at 0 °C and stirred at 0 °C for 3 h. Excess iodomethane (3.66 g, 25.79 mmol) was added via disposable syringe at 0 °C and stirred at 0 °C for 3 h. The ice–H_2O bath was then removed and the mixture was allowed to warm to room temperature. After stirring at room temperature overnight (ca. 10 h), the reaction mixture was quenched with H_2O (5 mL) at 0 °C. The mixture was stirred at room temperature for another 1 h and was then dried over anhydrous $MgSO_4$. The resulting mixture was concentrated under reduced pressure, and the concentrated mixture was chromatographed on silica gel to give α-methylbenzoin as a white solid (1.55 g, 87.7%): mp 65.5–66.5 °C (lit.[29] mp 66–67 °C); IR (KBr) 3300–3600 (br), 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.91 (s, 3 H), 4.79 (s, 1 H, D_2O exchangeable), 7.27–7.69 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 26.39, 79.38, 125.94, 128.14, 128.26, 128.94, 130.20, 132.86, 133.88, 142.71, 202.05.

Reductive Coupling of Benzoyl Chloride Using Activated Nickel. Activated nickel powder (7.46 mmol) was generated by stirring Li^0 (16.93 mmol), nickel(II) iodide (7.46 mmol), and naphthalene (0.75 mmol) in glyme (25 mL) at room temperature for 30 h. Benzoyl chloride (1.043 g, 7.42 mmol) was added dropwise via syringe at 0 °C, and the reaction mixture was stirred at room temperature for 36 h. The reaction was quenched with H_2O (5 mL), and CH_2Cl_2 (50 mL) was added. The mixture was washed with H_2O, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting mixture was chromatographed on silica gel to give benzil (180 mg, 23%) and *trans*-α,α'-stilbenediol dibenzoate (170 mg, 22%). Benzil: mp 94.0–94.5 °C; IR (KBr) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53 (t, 4 H), 7.68 (t, 2 H), 7.99 (d, 4 H). *trans*-α,α'-Stilbenediol dibenzoate: mp 188.5–189.0 °C (lit.[4] mp 189 °C); IR (KBr) 1740, 1595, 1490, 1445, 1255, 1235, 1115, 1080, 1030, 1010, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28 (m, 6 H), 7.48 (t, 4 H), 7.62 (t, 2 H), 7.67 (d, 4 H), 8.10 (d, 4 H); MS (EI) m/e (relative intensity) 421 (2.5), 420 (M^+, 9.1), 210 (0.1), 106 (7.5), 105 (100.0), 77 (27.6). Calcd for $C_{28}H_{20}O_4$ (M^+) m/e 420.1362, found m/e 420.1365.

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Epimerization and Oxidation of the Bridgehead Hydrogen of Some Indoloquinolizideines

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It has been known for a long time that the bridgehead, aminomethine hydrogen of indole alkaloids of the yohimboid, heteroyohimboid, and corynanthoid types (H-3 in formula 1, Chart I) can be epimerized in acid media.[1] In view of the general inefficiency of this process most isomerizations have been performed over the years by oxidation–reduction operations.[2] In light of this accumulated experience the recently reported,[3] facile, acid-induced **2a** → **2b** conversion was surprising and required further scrutiny. Since vinylogous urethanes of type **2a** have been the pivotal intermediates in syntheses of the aforementioned indole bases[4] and can be prepared easily by a two-step reaction sequence of carbon nucleophile addition to 1-tryptophyl-3-acylpyridinium salts and subsequent acid-induced ring closure (e.g., the **3a**[5] → **4** → **5** transformations described in detail in the Experimental Section), five vinylogous urethanes—**5**, **6**,[6] **7**,[6] **8b** (prepared from **8a**[6] on reduction with Raney nickel), and **9**[7]—were on hand for a study of their response to exposure to trifluoroacetic acid.

(1) Cf.: Gaskell, A. J.; Joule, J. A. *Tetrahedron* **1967**, *23*, 4053.
(2) Cf.: Weisenborn, F. L.; Diassi, P. A. *J. Am. Chem. Soc.* **1956**, *78*, 2022. Wenkert, E.; Roychaudhuri, D. K. *J. Org. Chem.* **1956**, *21*, 1315.
(3) Rosentreter, U.; Born, L.; Kurz, J. *J. Org. Chem.* **1986**, *51*, 1165.
(4) (a) Wenkert, E.; Chang, C.-J.; Chawla, H. P. S.; Cochran, D. W.; Hagaman, E. W.; King, J. C.; Orito, K. *J. Am. Chem. Soc.* **1976**, *98*, 3645; **1982**, *104*, 6166. (b) Wenkert, E.; Halls, T. D. J.; Kunesch, G.; Orito, K.; Stephens, R. L.; Temple, W. A.; Yadav, J. S. *Ibid.* **1979**, *101*, 5370; **1982**, *104*, 6166. (c) Wenkert, E.; Vankar, Y. D.; Yadav, J. S. *Ibid.* **1980**, *102*, 7971. (d) Wenkert, E.; Pyrek, J. St.; Uesato, S.; Vankar, Y. D. *Ibid.* **1982**, *104*, 2244. (e) Spitzner, D.; Wenkert, E. *Angew. Chem.* **1984**, *96*, 972.
(5) Wenkert, E.; Dave, K. G.; Haglid, F. *J. Am. Chem. Soc.* **1965**, *87*, 5461.
(6) Wenkert, E.; Angell, E. C.; Drexler, J.; Moeller, P. D. R.; Pyrek, J. St.; Shi, Y.-J.; Sultana, M.; Vankar, Y. D. *J. Org. Chem.* **1986**, *51*, 2995.
(7) This compound has been prepared by (a) treatment of the *N*-tryptophyl salt of ethyl β-(β-pyridyl)acrylate with sodium hydride, (b) exposure of the product first to ethylthioacetonitrile in dimethylsulfoxide solution and then to trifluoroacetic acid in methylene chloride solution, and (c) Raney nickel desulfurization of the resultant tetracyclic product (Wenkert, E.; Shi, Y.-J., unpublished observations).

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