69468-42-4; **20**, 85152-86-9; **21**, 85152-87-0; **22**, 6455-14-7; **23**, 71518-92-8; **24**, 85152-88-1; Se, 7782-49-2; phenyllithium, 591-51-5; *p*-dibromobenzene, 106-37-6; 1-bromonaphthalene, 90-11-9; *m*-bromotoluene, 591-17-3; furan, 110-00-9; thiophene, 110-02-1; benzo[*b*]thiophene, 95-15-8; bromomesitylene, 576-83-0; 2-bromopyridine, 109-04-6; diphenyl ether, 101-84-8.

Supplementary Material Available: Full IR, NMR, and mass spectral data for compounds **4** and **7–24** (5 pages). Ordering information is given on any current masthead page.

Syntheses and Structural Studies in the 4-Phenylbenzo[*g*]indolin-2-one System[1a]

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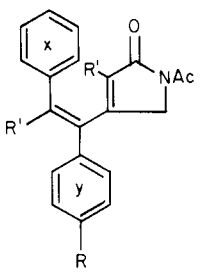
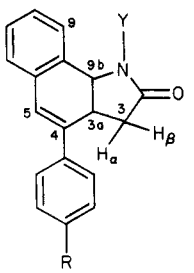
Received September 29, 1982

Acid-catalyzed deacetylation of unsaturated lactam **1** was accompanied by cyclization to yield 4-phenyl-3a,9b-dihydrobenzo[*g*]indolin-2-one (**4**; 71%), which adsorbed 1 mol of hydrogen to form **15**. Compound **15** was also obtained by intramolecular [4 + 2] cycloaddition of 1-[(4-phenyl-3-butynoyl)amino]cyclobutene **21** to give an isomer (**22**; 47%) of **4** and subsequent hydrogenation thereof. Chemical and spectral studies that led to structural elucidation of these compounds and some of their derivatives are presented.

In a preceding paper[2] we described the intramolecular cyclizations of *N*-(phenylpropargyl)-*cis*-cinnamamide in refluxing acetic anhydride to form (*Z*)-1-acetyl-4-(1,2-diphenylvinyl)-3-pyrrolin-2-one (**1**; resulting from [2 + 2] cycloaddition–cycloreversion), as well as [4 + 2] cycloaddition products. The bromo derivative **2** and the dideuterio derivative **3** were obtained analogously. Structural elucidations of **1–3** were reported previously.[2,3] The present paper concerns structural changes that **1–3** undergo during acid-catalyzed deacetylation.

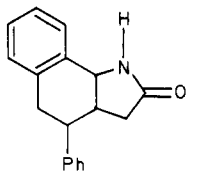




1, R = R' = H
2, R' = H; R = Br
3, R' = D; R = H

4, R = Y = H
5, R = H; Y = Ac
6, R = Br; Y = H
7, R = Br; Y = Ac

Deacetylation–Reacetylation Studies. Refluxing **1** (mp 132 °C) in aqueous hydrochloric and acetic acids effected deacetylation (71%) to yield a colorless compound (mp 214 °C, $C_{18}H_{15}NO$) that showed spectral and polarographic properties inconsistent with the expected **8** but which were indicative of a tricyclic indolinone structure **4** or an isoindolinone structure **14**. Also, reacetylation of the 214 °C compound with Ac_2O failed to regenerate **1**. Instead, it produced a new substance (shown to be **5**, $C_{20}H_{17}NO_2$, mp 143 °C), isomeric with **1** and reconvertible (61%) into the 214 °C compound on deacetylation in the aforementioned manner. Catalytic hydrogenation of the 214 °C compound produced a dihydro derivative (mp 205 °C) that lacked the stilbene chromophore and was presumed to be either **15** or **16**. While neither **4** nor **15** had



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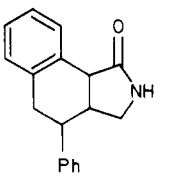

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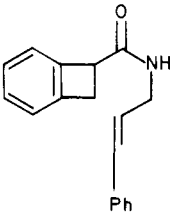

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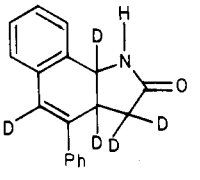
been reported previously, Oppolzer[4] had synthesized all of the four possible racemates of **16** by means of thermal cyclization of **17**. Our 205 °C compound was not identical with any of these racemates so that the isoindolinone structure **14** was eliminated as a possibility for our 214 °C product.

Similarly, deacetylation of bromo compound **2** (to **6**) and subsequent reacetylation formed **7**. The presence of a slightly distorted A_2B_2 multiplet ($J \simeq 8$ Hz) at δ 7.5 in the ^{1}H NMR spectrum of **7** indicated that cyclization had indeed occurred into ring x rather than into ring y.

H–D exchange experiments led to a rationalization for the conversion of **1** into **4**. Thus, when dideuterio **1** (i.e., **3**) was refluxed with HCl–HOAc–H_2O, the product (**4**) contained no deuterium atoms. Also, when **1** (or **3**) was refluxed with DCl–DOAc–D_2O (followed by H_2O workup), the 214 °C product was pentadeuterio **4** (i.e., **18**), wherein



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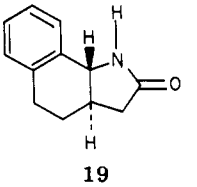

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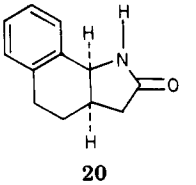

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all protons on aliphatic carbons had been exchanged. As a rationalization of the exchange processes, we invoked the

(1) (a) This investigation was supported in part by research grant GM 12730 from the National Institutes of General Medical Sciences, U.S. Public Health Service. (b) Graduate Teaching and Research Assistant, 1969–1973. (c) Undergraduate Teaching and Research Assistant, 1978–1980.

(2) Klemm, L. H.; Hwang, Y. N.; McGuire, T. M. *J. Org. Chem.* **1976**, *41*, 3813.

(3) Weaver, L. H.; Hwang, Y. N.; Matthews, B. W. *Acta Crystallogr., Sect. B* **1974**, *30*, 2775.

(4) We thank Dr. Wolfgang Oppolzer for kindly furnishing copies of ^{1}H NMR spectra from his unpublished studies. For examples of similar intramolecular [4 + 2] cycloadditions, see Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10; *Synthesis* **1978**, 793.

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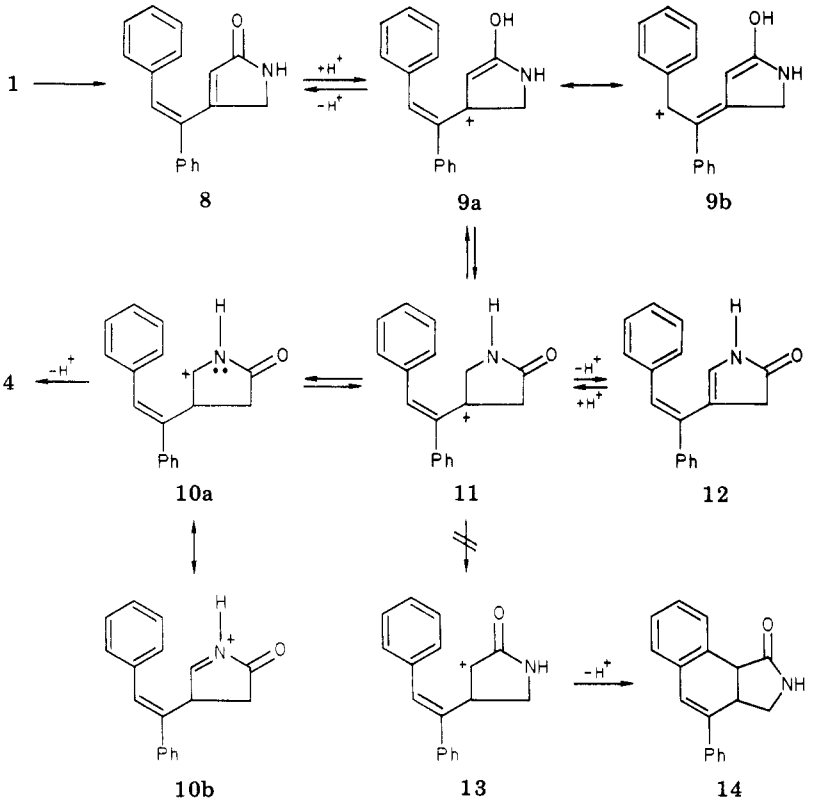
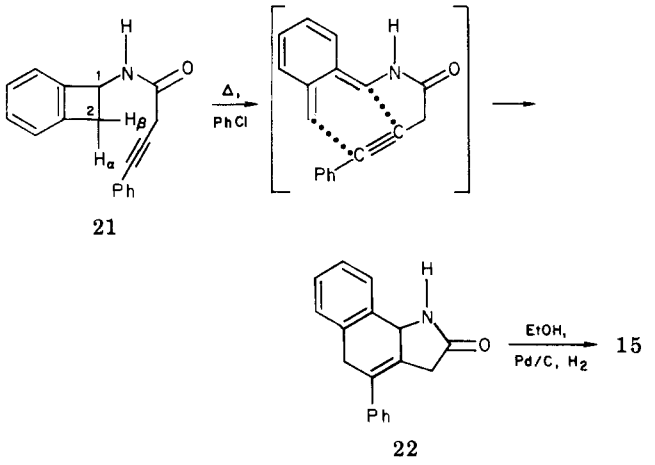
Scheme I. Proposed Mechanistic Steps for the Conversion of 1 into 4



mechanistic steps shown in Scheme I, where one effectively obtains equilibration between intermediates **8** and **12** during acid-catalyzed cyclization (i.e., S_E reaction) into ring x. Protonation of **8** most likely would occur on oxygen to give the resonance-stabilized carbocation **9**, convertible to the keto form **11**. Hydride shift in **11** could give either resonance-stabilized **10**, the precursor of **4**, or the less stable (more highly energetic) **13**, the expected precursor of **14**. The failure to isolate **14** implies that **13** (plus charge α to a carbonyl group) does not form in the hydrolysis mixture. One can then account for the observations on H–D exchange by assuming that all allylic hydrogen atoms in **8**–**12** are exchangeable during the transformations of Scheme I.

Unequivocal Synthesis of 15. As conclusive proof that our 205 °C compound has structure **15**, we synthesized **15** via the structurally unequivocal intramolecular Diels–Alder pathway shown in Scheme II. Unsaturated amide **21** was obtained (79%) from Schotten–Baumann condensation of 1-aminobenzocyclobutene hydrochloride with 4-phenyl-3-butynoyl chloride. The structure of **21** was confirmed by ^{1}H NMR and UV spectral investigations. Thermal [4 + 2] cycloaddition of **21** proceeded in chlorobenzene at 132 °C to produce **22** (47%, mp 232 °C), an isomer of **4**. Assignment of the position of the carbon–carbon double bond in **22** is based on the proposed mechanism of cyclization,[4] closeness of the UV spectra of **22** (λ_{max} 247 nm, log ϵ 4.04) and styrene (248, 4.15),[5] a decreased rate of catalytic hydrogenation of **22** (tetrasubstituted alkene) as compared to that of **4** (trisubstituted alkene) under the same conditions.[6] and the presence of a one-proton signal at δ 5.18 for H-9b.[7]

Scheme II. Synthetic Pathway to Authentic 15



Originally we had hoped that cyclization of **21** might be accompanied by double-bond migration to yield **4** (rather than **22**) directly. Since this did not occur, we attempted (without success) to isomerize **22** to **4** by refluxing the former in the deacetylating mixture that served to convert **1** into **4**. Because of the possibility that catalytic hydrogenations of **4** and **22** would lead to different stereoisomers, the transformation **22** → **15** was approached with some trepidation. Fortunately for this structural proof, however, identical products were obtained in both cases. In fact, ^{1}H NMR examination of the crude hydrogenation products from both **4** and **22** failed to reveal the presence of isomeric components. As a synthetic route to **15**, it is clear that the

(5) Gillam, A. E.; Stern, E. S. "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry"; 2nd ed.; Edward Arnold: London, 1960; p 277.

(6) Rimek, H.-J. In "Houben-Weyl, Methoden Der Organischen Chemie", 4th ed.; Georg Thieme: Stuttgart, 1980; Vol. IV/1c; pp 146–148.

(7) If the double bond had migrated to the 3a,9b-position, this signal (for H-4) should appear at ca. δ 2.8.[8a]

(8) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; (a) p 220, (b) p 205.

sequence starting from 1 is considerably more facile than that of Scheme II since the former route involves more readily available precursors.

At this point, the stereochemistries of 4–7 and 15 remain uncertain. The identical coupling constants of $J_{3a,9b}$ = 8 Hz in 4–7 indicate that all of these compounds have the same stereochemical juncture for the lactam ring. This geometry is probably retained on catalytic hydrogenation, for $J_{3a,9b}$ is 7.7 Hz in 15. However, confusion between cis and trans ring junctures remains when one compares these J values with those reported by Oppolzer[9] for the dephenyl derivatives (19, 20) of 15, i.e., 8.5 Hz and 6.5 Hz, respectively. Likewise, the observation of Siegel and Smith[10] that catalytic hydrogenation of substituted cyclohexenes by means of Pd/C in EtOH may give the more stable product (rather than the one from syn addition) does not simplify the problem.

Experimental Section[11]

Deacetylation of 1. A mixture of 1.76 g of (*Z*)-1-acetyl-4-(1,2-diphenylvinyl)-3-pyrrolin-2-one (1;[2] mp 131–132 °C), 1 L of glacial HOAc, 30 mL of concentrated hydrochloric acid, and 30 mL of H_2O was refluxed for 8 h. Concentration of the solution gave a yellow-brown viscous liquid, which crystallized on cooling. Recrystallization from EtOH produced 1.08 g (71%) of colorless or pale-yellow prisms of 4-phenyl-3a,9b-dihydrobenzo[g]indolin-2-one (4): mp 212–214 °C dec; IR ($CHCl_3$) 3430 (w, NH), 1690 (s, C=O) cm^{-1}; IR (KBr) 1675 (s, C=O), 810 (m, C=CH), 760, 690 (s, Ph) cm^{-1}; UV (absolute EtOH) λ_{max} 231 nm (log ϵ 4.09); 237 (4.08), 303 (4.25), 313 (sh, 4.18), 330 (sh, 3.79);[12] ^1H NMR (C_6D_5N) δ 9.32 (br, NH; disappears on addition of D_2O), 7.7–7.0 (m, 9 aromatic H), 6.86 (s, 1, H-5), 5.12 (d, $J_{3a,9b}$ = 8 Hz, 1, H-9b), 3.89 (pseudoquartet, J = 8 Hz, 1, H-3a), 2.80 (dd, J_{gem} = 16 Hz, $J_{3\alpha,3a}$ = 8 Hz, 1, H-3α), 2.38 (dd, J_{gem} = 16 Hz, $J_{3\beta,3a}$ = 8 Hz, 1, H-3β); double irradiation at δ 5.12 changed only the pseudoquartet, 3.89 (t, $J_{3,3a}$ = 8 Hz); double irradiation at δ 3.89 gave three changes, 5.12 (s), 2.80 (d, J_{gem} = 16 Hz), 2.38 (d, J = 16 Hz); $E_{1/2}$ = –2.21, –2.39 V;[13] mass spectrum, m/e (relative intensity) 262 (21), 261 (100, M^+), 260 (42), 217 (23, $M^+ - H_2NCO$), 215 (16).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.74; H, 5.77; N, 5.36.

Acetylation of 4. A solution of 101 mg of 4 in 100 mL of Ac_2O was refluxed for 6 h, concentrated in vacuo, and cooled to 25 °C. Precipitated *N*-acetyl lactam 5 was filtered, washed with cold EtOH (yield 89 mg, 76%), and recrystallized from EtOH to give needles: mp 142–143 °C; IR ($CHCl_3$) 1740, 1695 (s, AcNC=O) cm^{-1}; UV (absolute EtOH) λ_{max} 227 nm (log ϵ 3.85), 233 (sh, 3.82), 304 (3.86), 316 (3.85), 330 (sh, 3.58); ^1H NMR ($CDCl_3$) δ 7.6–7.1 (m, 9 aromatic H), 6.88 (s, 1, H-5), 6.00 (d, $J_{3a,9b}$ = 8 Hz, 1, H-9b), 3.54 (dt, $J_{3\alpha,3a} = J_{3a,9b}$ = 8 Hz, $J_{3\beta,3a}$ = 12 Hz, 1, H-3a), 2.70 (s, 3, Ac) superimposed on 2.8–2.6 (m, 2, H-3α and H-3β); double irradiation at δ 6.00 changed only the d of t, 3.54 (dd, $\Delta\delta$ = 8.9 Hz); double irradiation at δ 3.54 gave two changes, 6.00 (s), 2.8–2.6 (modified splitting pattern); double irradiation at ca. δ 2.70 changed only the d of t, 3.54 (d, $J_{3a,9b}$ = 8 Hz); ^{13}C FT NMR ($CDCl_3$)[15] δ 175.0 and 172.2 (2 C=O), 139.1–124.1 (≥ 11 aromatic and vinylic C), 59.2 (d, C-9b), 39.5 (t, C-3), 36.9 (d, C-3a), 26.1 (q, CH_3C=O); $E_{1/2}$ = –2.14, –2.38, –2.58 V;[13] mass spectrum, m/e (relative intensity) 303 (83, M^+), 261 (99, $M^+ - CH_2CO$), 260 (34, M^+ – Ac), 219 (100, $M^+ - 2CH_2CO$, HR), 218 (41, M^+ – AcNC=O, HR), 178 (4, $C_{14}H_{10}^+$, HR), 43 (32, Ac^+).

Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.18; H, 5.65; N, 4.62. Found: C, 79.56; H, 5.68; N, 4.31.

Plots of chemical shifts induced on individually identifiable proton signals in the ^1H NMR spectrum ($CDCl_3$) of 5 were linear over the range of 0.25–0.75 for the molar ratio of tris(dipivalomethanato)europium(III):5. Slopes found were CH_3CO, 7.7; H-3, 4.6; H-3a, 3.3; H-5, 1.5; H-9, 6.1; H-9b, 6.3, which were consistent with coordination of the europium ion onto the oxygen atom of the acetyl group.

Deacetylation of Bromo Compound 2. As in the conversion 1 → 4, 1.03 g of 2 produced 0.52 g (57%) of needles of 6: mp 242–244 °C dec; IR (KBr) 1685 (s, C=O), 825, 810, 755, 710 cm^{-1}; ^1H NMR (C_6D_5N) δ 9.36 (br, NH), 7.6–7.1 (m, 8 aromatic H), 6.90 (s, 1, H-5), 5.13 (d, $J_{3a,9b}$ = 8 Hz, 1, H-9b), 3.84 (pseudoquartet, J = 8 Hz, 1, H-3a), 2.83 (dd, J_{gem} = 16 Hz, $J_{3\alpha,3a}$ = 8 Hz, 1, H-3α), 2.34 (dd, J_{gem} = 16 Hz, $J_{3\beta,3a}$ = 8 Hz, 1, H-3β); mass spectrum, m/e (relative intensity) 341 (98, M^+), 340 (49), 339 (100, M^+), 338 (32), 217 (24), 216 (21, M^+ – [HNCO + HBr]), 215 (28), 202 (25, $M^+ - [HNCOCH_2 + HBr]$).

Anal. Calcd for $C_{18}H_{14}BrNO$: C, 63.54; H, 4.15; N, 4.12. Found: C, 63.42; H, 4.35; N, 3.91.

Acetylation of Bromo Compound 6. A solution of 202 mg of 6 in 175 mL of Ac_2O was refluxed for 5 h in a nitrogen atmosphere. Concentration of the solution and refrigeration (–10 °C) gave 184 mg (81%) of needles (EtOH) of 7: mp 180–181.5 °C; ^1H NMR ($CDCl_3$)[16] δ 7.7–7.3 (distorted A_2B_2 system $J_{AB} \simeq$ 8.2 Hz, 4 aromatic H in ring y), which overlaps 7.35–7.1 (m, 4 aromatic H in ring x), 6.88 (s, 1, H-5), 6.01 (d, $J_{3a,9b}$ = 8 Hz, 1, H-9b), 3.49 (dt, $J_{3\alpha,3a} = J_{3a,9b}$ = 8 Hz, $J_{3\beta,3a}$ = 12 Hz, 1, H-3a), 2.68 (s, Ac) superimposed on 2.9–2.4 (m, 5 total, 2 H-3).

Anal. Calcd for $C_{20}H_{16}BrNO_2$: C, 62.84; H, 4.22; N, 3.67. Found: C, 63.02; H, 4.28; N, 3.52.

Deacetylation of 3 in Deuterated Solvent. Refluxing 180 mg of dideuterio compound 3 in a mixture of 100 mL of DOAc (Diaprep) and 7 mL of 20% DCl in D_2O (Diaprep; as in deacetylation of 1) plus evaporation of the solvent produced 77 mg (49%) of needles (EtOH) of pentadeuterio compound 18: mp 213–214 °C, ^1H NMR (C_6D_5N) δ 9.28 (br, NH), 7.6–7.0 (m, aromatic protons); mass spectrum, m/e (relative intensity) 267 (24), 266 (100, M^+), 265 (49, M^+ – H, HR), 264 (22, M^+ – D, HR), 222 (19, $M^+ - H_2NCO$), 221 (17, M^+ – DHNCO), 220 (10), 219 (10), 208 (10), 205 (9).

Anal. Calcd for $C_{18}H_{10}D_5NO$: 33.3 atomic % excess D. Found:[17] 30.9 atomic % excess D.

Hydrogenation of 4. A solution of 491 mg of 4 in 150 mL of 95% ethanol at 60 °C was cooled to 25 °C and shaken with 193 mg of 5% Pd/C under hydrogen gas at 3 atm pressure for 1 h.[18] Evaporation of the filtered mixture and recrystallization of the residue from ethanol gave 276 mg (56%) of prisms of 4-phenyl-3a,4,5,9b-tetrahydrobenzo[g]indolin-2-one (15): mp 203–205 °C; IR ($CHCl_3$) 3440 (w, NH), 1690 (s, C=O) cm^{-1}; IR (KBr) 1690 (s, C=O), 690, 765 (s, Ph) cm^{-1}; UV (absolute EtOH)

(9) Oppolzer, W. *J. Am. Chem. Soc.* **1971**, *93*, 3833.
(10) Siegel, S.; Smith, G. V. *J. Am. Chem. Soc.* **1960**, *82*, 6087.
(11) Elemental analyses were determined by MHW Laboratories, Garden City, MI, or by Drs. Susan Rottschaefer and Richard E. Wielesek of this laboratory. High- and low-resolution mass spectra were also obtained by Rottschaefer and Wielesek by means of a CEC Model 21-110 double-focusing instrument operated at 70 eV. Mass spectral peaks confirmed by high-resolution studies are designated HR. Infrared spectra were obtained by means of Beckman IR-5, IR-7, or IR-10 instruments; ultraviolet spectra by means of a Cary Model 15 spectrophotometer, ^1H NMR spectra by means of Varian HA-100 and XL-100 instruments with tetramethylsilane as internal standard.
(12) This spectrum closely resembles that of *trans*-stilbene. Jaffe, H. H.; Orchin, M. "Theory and Applications of Ultraviolet Spectroscopy"; Wiley: New York, 1962; p 425.
(13) Polarographic half-wave reduction potentials vs. the saturated calomel electrode (SCE). Polarograms were obtained in anhydrous MeCN–Et_4NBr as the solvent–electrolyte in the manner described previously. Klemm, L. H.; Olson, D. R. *J. Org. Chem.* **1979**, *44*, 4524. The first reduction wave of 4 is close to that predicted for *trans*-stilbene under the same reaction conditions[14] and markedly more negative than that measured (–1.53 V) for 1.[2]
(14) The first reduction wave for *trans*-stilbene in MeCN–0.1 M *n*-Bu_4NI is reported to be –1.73 V (vs. a Hg pool). In DMF–*n*-Bu_4NI values reported are –1.64 (vs. a Hg pool) and –2.21 V (vs. SCE). Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1970; p 50. Assuming that the difference of –0.57 V between reference electrodes in DMF also holds in MeCN, one estimates $E_{1/2}$ = –2.30 V (vs. SCE) for *trans*-stilbene under our polarographic conditions.
(15) Determined on a Varian HA-100 instrument with deuterium lock. δ values were measured vs. the central peak for $CDCl_3$ (taken as 76.9 ppm vs. Me_4Si) and are referred to Me_4Si as a standard. Multiplicities were obtained from off-resonance studies.
(16) Combined data from 60-MHz CW and 100-MHz FT spectra.
(17) Analysis by Josef Nemeth, Urbana, IL.
(18) The same product was obtained when the shaking was continued for 10 h.

λ_{max} 247 nm (log ϵ 1.94), 252 (2.07), 257 (2.19), 263 (2.22), 267 (sh, 2.11), 271 (2.11); ^{1}H NMR ($CDCl_3$)[19] δ 7.5–7.0 (m, 10, aromatic protons plus NH), 4.94 (d, $J_{3a,9b}$ = 7.7 Hz, 1,H-9b), 3.6–2.6 (m, 4, H-3a, H-4, 2 H-5), 2.36 (dd, $J_{3a,3\alpha}$ = 9.2 Hz, $J_{3\alpha,3\beta}$ = 17.2 Hz, 1, H-3α), 2.04 (dd, $J_{3a,3\beta}$ = 9.0 Hz, $J_{3\alpha,3\beta}$ = 17.2 Hz, 1, H-3β); double irradiation at δ 3.23 (approximate resonance for H-3a) produced three changes, 4.94 (s), 2.36 (d, $J_{3\alpha,3\beta} \simeq$ 17 Hz), 2.04 (d, $J \simeq$ 17 Hz); mass spectrum, m/e (relative intensity) 263 (19, M^+), 261 (21), 205 (26), 204 (100, M^+ – [2H + CH_2CONH], HR), 159 (53, M^+ – PhCH=CH_2, HR), 117 (29), 115 (32), 91 (44, $C_7H_7^+$), 77 (20, Ph^+).

Anal. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.15; H, 6.51; N, 5.19.

Benzocyclobuten-1-aminium Chloride.[20] To a stirred solution of 3 g (20 mmol) of benzocyclobutene-1-carboxylic acid[21] in 40 mL of $CHCl_3$ (nitrogen atmosphere) were added 9 mL of concentrated H_2SO_4 and then, dropwise, 28 g of standardized 3.76% (w/w; 24 mmol) HN_3 in $CHCl_3$[22] at such a rate that bubbling was vigorous. Stirring was continued 1.5 h longer and the mixture was poured into 70 mL of cold, aqueous 10% NaOH solution. The solution was made strongly basic with more NaOH, extracted twice with ether, saturated with NaCl, and extracted twice more with ether. Combined ether layers were dried (Na_2SO_4) and treated with dry HCl gas. The white precipitate was collected by filtration (brown oil discarded) and dried in a desiccator, yield 1.96 g (63%), mp 179–181 °C (lit.[23] mp 185.5–187 °C).

1-[(4-Phenyl-3-butynoyl)amino]benzocyclobutene (21). To a solution of 2.5 g (15.6 mmol) of 4-phenyl-3-butynoic acid [mp 70–71 °C, prepared from 4-phenyl-3-butyn-1-ol (Farchan) by oxidation in 10 stages as reported by Alekseeva et al.[24]] in 125 mL of dry benzene was added 3.71 g (31.2 mmol) of thionyl chloride, and the mixture was refluxed for 3 h in an atmosphere of nitrogen. Volatile components of the mixture were removed by repeated rotoevaporation and dilution with benzene (four times). Solutions of the residual acid chloride in 60 mL of benzene and 16 mL (32 mmol) of 2 M aqueous NaOH were added dropwise simultaneously to a vigorously stirred suspension of 1.96 g (12.6 mmol) of preceding benzocyclobuten-1-aminium chloride in 50 mL of benzene in an atmosphere of nitrogen. After additional stirring (3 h), the benzene layer was washed successively with water, 5% hydrochloric acid, 5% aqueous Na_2CO_3, and water and evaporated to dryness. The residue was chromatographed with chloroform–silica gel to yield 2.63 g (80%) of **21** (mp 143–144 °C), converted to needles after recrystallizations from aqueous MeCN (1:5.3) and 95% EtOH: mp 147–148 °C; IR ($CHCl_3$) 3390 (m, NH), 1670 (s, C=O) cm^{-1}; IR (KBr) 3240 (m, NH), 1650 (C=O), 750, 690 (Ph) cm^{-1}; UV (95% EtOH) λ_{max} 238.8 nm (log ϵ 4.32), 249.2 (4.31), 264.2 (3.50), 270.8 (3.46), 277.6 (2.86), 287.5 (2.32);[25] ^{1}H NMR ($CDCl_3$, degassed) δ 7.4–6.8 (m, 10, aromatic protons plus NH shoulder at ca. 6.96), 5.52 (pseudoseptet, $J_{1,NH}$ = 8.0 Hz, $J_{1,2\alpha}$ = 4.9 Hz, $J_{1,2\beta}$ = 2.3 Hz, 1, H-1), 3.72 (dd, $J_{2\alpha,2\beta}$ = 14.5 Hz, 1, H-2α), 3.45 (s, 2, CH_2C=O), 3.04 (dd, 1, H-2β);[28] double irradiation at δ 5.52 changed the signal at 3.04 to a doublet, $J_{2\alpha,2\beta}$ = 14.5 Hz and caused partial collapse of the d of d at 3.72; double irradiation at δ 6.96 changed the signal at 5.52 to a broad, unresolved peak; mass spectrum, m/e (relative intensity) 261 (34, M^+), 260 (94), 184 (97, M^+ – Ph), 146 (60), 119 (42), 118 (52), 115 (100, PhC≡CCH_2^+), 103 (40).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.35; H, 5.67; N, 5.08.

4-Phenyl-5,9b-dihydrobenzo[*g*]indolin-2-one (22). A solution of 1.01 g of amide **21** in 50 mL of freshly distilled chlorobenzene was refluxed in an atmosphere of nitrogen for 17 h. The cooled solution deposited needles that were dried in vacuo, yield 0.47 g (47%), and sublimed at 150 °C (0.03 mm) to give **22**: mp 227–232 °C dec; IR ($CHCl_3$) 1700 (C=O) cm^{-1}; IR (KBr) 3180 (w, NH), 1700 (C=O), 760, 700 (Ph) cm^{-1}; UV (absolute EtOH) λ_{max} 247 nm (log ϵ 4.04); ^{1}H NMR ($CDCl_3$) δ 8.01 (s, 1, NH), 7.6–7.2 (m, 9, aromatic protons), 5.18 (d, J = 4 Hz, 1 H-9b), 4.0–2.9 (m, 4, 2 H-3 plus 2 H-5); mass spectrum, m/e (relative intensity) 262 (24), 161 (100, M^+), 260 (54), 259 (50), 230 (26), 215 (29), 184 (62, M^+ – Ph).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.63; H, 5.75; N, 5.28.

Hydrogenation of 22. Use of the same procedure as used in hydrogenation of **4** except that the reaction time was 10 h gave a first crop of plates (73%; mp 203–204 °C) from EtOAc, converted to prisms (mp 204–206 °C) on recrystallization from ethanol. The product was shown to be identical with **15** (from **4**, vide supra) by mixture melting point and spectral methods.

Acknowledgment. We express our appreciation to Dr. Daniel R. Olson who obtained polarograms on **4** and **5** and to Dr. Ronald E. Merrill who determined the ^{13}C NMR spectrum of **5**.

Registry No. 1, 60224-37-5; **2**, 54153-66-1; **3**, 60224-39-7; **4**, 85097-27-4; **5**, 85097-28-5; **6**, 85097-29-6; **7**, 85097-30-9; **15**, 85097-32-1; **18**, 85097-31-0; **21**, 85097-33-2; **22**, 85097-34-3; benzocyclobuten-1-amine hydrochloride, 2299-00-5; benzocyclobutene-1-carboxylic acid, 14381-41-0; 4-phenyl-3-butynoic acid, 7218-49-7; 4-phenyl-3-butynoic acid chloride, 17066-23-8.

(19) Spectral data were analyzed with the aid of the computer program NTCSIM (Nicolet Magnetics Corp.) for NMR simulation.

(20) This is an improved modification of the procedure that was reported by Horner, L.; Kirmse, W.; Muth, K. *Chem. Ber.* **1958**, *91*, 430.

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(25) Corroboration of the structure of **21** was obtained by comparison of its plotted UV spectrum with a summation spectrum for benzocyclobutene[26] and phenylacetylene.[27] The two plots are closly similar in shape and log ϵ values, except that the spectrum of **21** is (as expected) displaced bathochromically by ca. 5 nm in the positions of the maxima in the short-wavelength region (220–255 nm).

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(28) The protons at C-1 and C-2 were treated as an AMX system[8b] in computational frequency analysis. J_{gem}, $J_{1,2\alpha}$, and $J_{1,2\beta}$ are reported as 14.6, 4.76, and 1.95 for 1-bromobenzocyclobutene[29] and 14, 5.5, and 2.5, respectively, for 1-cyanobenzocyclobutene.[30]

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(30) Klundt, I. L. *Chem. Rev.* **1970**, *70*, 471. See p 486. It might be noted that assignments of J_{cis} and J_{trans} in ref 29 and 30 are not consistent with one another. Our use of α and β designations circumvents the question of stereochemistry here.