Evaporation of the filtrate, chromatography of the residue on silica gel impregnated with 20% silver nitrate, and elution with 33:1 hexane–ethyl acetate gave 600 mg (15%) of colorless, liquid 1,4,4-trimethyl-9-*endo*-vinylbicyclo[3.2.2]non-6-en-2-one (**8a**): IR C=O 1705 (s), C=C 1652 (w) cm^{-1}; ^1H NMR δ 1.01, 1.06, 1.07 (s, 3 each, methyls), 1.42 (ddd, 1, J = 14, 5, 5 Hz, H-9), 2.21 (br dd, 1, J = 8, 5 Hz, H-5), 2.29 (dd, 1, J = 13, 1, Hz, H-3), 2.45 (dd, 1, J = 14, 10 Hz, H-9), 2.52 (d, 1, J = 13 Hz, H-3), 2.61 (ddd, 1, J = 10, 10, 5 Hz, H-8), 4.8–5.0 (m, 2, olefinic CH_2), 5.49 (ddd, 1, J = 17, 10, 10 Hz, α-H), 5.58 (d, 1, J = 9 Hz, H-7), 6.27 (dd, 1, J = 9, 8 Hz, H-6); ^{13}C NMR δ 20.4 (1-Me), 27.8 (4-Me), 29.8 (4-Me), 30.3 (C-9), 39.3 (C-4), 42.9 (C-5), 47.2 (C-8), 50.6 (C-1), 54.1 (C-3), 113.5 (β-C) 132.1 (C-7), 135.9 (C-6), 141.6 (α-C), 208.8 (C-2); MS, m/e 204 (M^+, 31), 160 (36), 159 (31), 148 (25), 145 (34), 133 (25), 120 (22), 119 (base), 105 (60), 92 (20), 91 (44), 77 (23).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.29; H, 9.87. Found: C, 82.36; H, 9.90.

Ketones 7b, 7c, and 8b. The cycloaddition of eucarvone (**1**) and (*E*)-1-methoxy-1,3-butadiene (**4b**) was carried out (heating at 180 °C for 60 h) in the same manner as the above thermal **1**–**4a** reaction, leading to a 3.4:2:1 **7b**–**8b**–**7c** adduct mixture in 47% yield (by GC analysis).

11α-Methoxy-1β,4,4-trimethylbicyclo[5.4.0]undeca-5,9-dien-2-one (7b): mp 74–75 °C (C_6H_{14}-EtOAc); IR olefinic CH 3010 (w), C=O 1702 (s), C=C 1650 (w) cm^{-1}; ^1H NMR δ 1.04, 1.11, 1.12 (s, 3 each, methyls), 2.13 (d, 1, J = 11 Hz, H-3), 2.18 (dd, 1, J = 17, 5 Hz, H-8), 2.39 (dm, 1, J = 11 Hz, H-8), 3.22 (br s, 1, H-7), 3.36 (s, 3, OMe), 3.47 (d, 1, J = 11 Hz, H-3), 3.77 (br d, 1, J = 4 Hz, H-11), 5.20 (dd, 1, J = 12, 2 Hz, H-5), 5.27 (dd, 1, J = 12, 3 Hz, H-6), 5.80 (ddd, 1, J = 10, 5, 2 Hz, H-9), 5.9–6.0 (m, 1, H-10); ^{13}C NMR δ 23.6 (1-Me), 27.6 (4-Me), 29.5 (C-8), 31.6 (4-Me), 33.5 (C-7), 37.2 (C-4), 51.0 (C-3), 55.9 (C-1), 58.3 (OMe), 78.6 (C-11), 124.9 (C-10), 125.6 (C-9), 129.4 (C-6), 137.6 (C-5), 214.2 (C-2); MS, m/e 234 (M^+, 1), 91 (18), 84 (base), 69 (22).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.87; H, 9.47. Found: C, 76.90; H, 9.50.

9-*endo*-[(*E*)-β-Methoxyvinyl]-1,4,4-trimethylbicyclo[3.2.2]non-6-en-2-one (8b): colorless liquid; IR olefinic CH 3030 (w), C=O 1685 (s), C=C 1648 (m) cm^{-1}; ^1H NMR δ 1.08 (s, 3, 4-Me), 1.10 (s, 3, 4-Me), 1.25 (s, 3, 1-Me), 1.48 (ddd, 1, J = 14, 5, 4 Hz, H-9), 2.26 (br dd, 1, J = 8, 5 Hz, H-5), 2.5–2.6 (m, 3, H-3, H-8, H-9), 2.69 (d, 1, J = 13 Hz, H-3), 3.52 (s, 3, OMe), 4.54 (dd, 1, J = 13, 10 Hz, α-H), 5.72 (d, 1, J = 9 Hz, H-7), 6.27 (d, 1, J = 13 Hz, β-H), 6.36 (dd, 1, J = 9, 8 Hz, H-6); ^{13}C NMR δ 21.2 (1-Me), 28.3 (4-Me), 29.3 (4-Me), 32.3 (C-9), 39.3 (C-4), 41.8 (C-8), 43.1 (C-5), 52.0 (C-1), 54.6 (C-3), 55.9 (OMe), 107.5 (α-C), 132.7 (C-7), 136.0 (C-6), 146.6 (β-C), 210.7 (C-2); MS, m/e 234 (M^+, 9), 84 (base), 69 (18).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.87; H, 9.47. Found: C, 76.80; H, 9.45.

11β-Methoxy-1β,4,4-trimethylbicyclo[5.4.0]undeca-5,9-dien-2-one (7c): colorless liquid; IR C=O 1710 (s), C=C 1670 (m) cm^{-1}; ^1H NMR δ 1.11, 1.12, 1.14 (s, 3 each, methyls), 1.99 (dm, 1, J = 19 Hz, H-8), 2.33 (d, 1, J = 11 Hz, H-3), 2.46 (dm, 1, J = 19 Hz, H-8), 2.9–3.0 (m, 1, H-7), 3.01 (d, 1, J = 11 Hz, H-3), 3.45 (s, 3, OMe), 3.92 (br s, 1, H-11), 5.27 (dd, 1, J = 12, 5 Hz, H-6), 5.33 (d, 1, J = 12 Hz, H-5), 5.6–5.7 (m, 2, H-9, H-10); ^{13}C NMR δ 17.4 (1-Me), 29.0 (C-8), 29.3 (4-Me), 31.3 (4-Me), 37.1 (C-4 or C-7), 37.3 (C-7 or C-4), 50.9 (C-3), 55.8 (C-1), 57.2 (OMe), 76.8 (C-11), 125.3 (C-10), 127.0 (C-9), 130.7 (C-6), 139.8 (C-5), 213.7 (C-2); MS, m/e 234 (M^+, 1), 84 (base), 69 (30).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.87; H, 9.47. Found: C, 76.92; H, 9.48.

A solution of 2.80 g (18.9 mmol) of eucarvone (**1**) in 20 mL of dry toluene was added to a solution of 9.90 g (9.4 mmol) of $Yb(fod)_3$ in 40 mL of dry toluene, and the mixture stirred under nitrogen at room temperature for 40 min. A solution of 9.42 g (112 mmol) of (*E*)-1-methoxy-1,3-butadiene (**4b**) in 23 mL of dry toluene was added, the heating tube degassed and sealed, and the solution heated at 110 °C for 168 h. The cooled mixture was poured into ice water, and the aqueous layer extracted with ether. The toluene and ether solutions were combined, washed with 10% sodium bicarbonate solution, dried (Na_2SO_4), and evaporated under vacuum. Chromatography of the residue, a 3.3:1.2:1 **7b**–**8b**–**7c** mixture (66%, by GC analysis), on 220 g of silica gel and elution with 9:1 hexane–ethyl acetate afforded 1.55 g (35%) of ketone **7b**, 400 mg (9%) of enol ether **8b**, and 300 mg (7%) of ketone **7c**.

Keto Aldehyde 9. Perchloric acid (1.3 mL, 50%) was added slowly to a solution of 50 mg (0.22 mmol) of enol ether **8b** in 13 mL of ether under nitrogen at 0 °C, and the mixture then stirred at room temperature for 2 h. The solution was poured into a mixture of pentane and water, and the aqueous layer extracted with pentane. The combined pentane solutions were washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed and eluted with 20:1 hexane–ethyl acetate, giving 46 mg (98%) of colorless, liquid keto aldehyde **9**: IR olefinic CH 3020 (w), C=O 1718 (s), 1686 (s), C=C 1648 (w) cm^{-1}; ^1H NMR δ 1.00, 1.06, 1.17 (s, 3 each, methyls), 1.1–1.3 (m, 2, H-8, H-9), 2.19 (dd, 1, J = 8, 6 Hz, H-5), 2.30 (d, 1, J = 13Hz, H-3), 2.31 (ddd, 1, J = 15, 10, 2 Hz, α-H), 2.4-2.7 (m, 2, H-9, α-H), 2.55 (d, 1, J = 13 Hz, H-3), 5.56 (d, 1, J = 9Hz, H-7), 6.26 (dd, 1, J = 9, 8 Hz, H-6), 9.78 (dd, 1, J = 2, <1 Hz, CHO); ^{13}C NMR δ 19.7 (1-Me), 27.8 (4-Me), 29.3 (4-Me), 30.1 (C-8), 35.3 (C-9), 39.5 (C-4), 42.6 (C-5), 49.3 (α-C), 50.9 (C-1), 54.0 (C-3), 131.7 (C-7), 136.2 (C-6), 202.0 (CHO), 208.5 (C-2); MS, m/e 220 (M^+, 1), 176 (32), 175 (34), 133 (69), 120 (60), 119 (60), 105 (35), 93 (52), 92 (base), 91 (85), 77 (45).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.20; H, 9.15.

***cis*-11α-Methoxy-1β,4,4-trimethylbicyclo[5.4.0]undecan-2-one (10).** A mixture of 230 mg (0.99 mmol) of ketone **7b** and platinum (preformed on hydrogenation of 230 mg of platinum oxide) in 13 mL of dry ethanol was hydrogenated at room temperature and atmospheric pressure. The mixture was filtered, and the filtrate evaporated. Chromatography of the residue and elution with hexane afforded 230 mg (97%) of colorless liquid ketone **10**: IR C=O 1700 (s) cm^{-1}; ^1H NMR δ 0.91, 0.98, 1.00 (s, 3 each, methyls), 1.2–1.9 (m, 10, methylenes), 2.00 (dd, 1, J = 11, 2 Hz, H-3), 2.5–2.7 (m, 1, CH), 2.80 (d, 1, J = 11 Hz, H-3), 3.25 (s, 3, OMe), 3.67 (br s, 1, H-11); ^{13}C NMR δ 15.5 (C-9), 23.7 (C-8), 24.3 (1-Me), 24.3 (4-Me), 29.5 (C-6), 30.5 (C-10), 33.7 (4-Me), 33.9 (C-4), 40.9 (C-7), 45.3 (C-5), 52.9 (C-3), 53.5 (C-1), 57.4 (OMe), 80.4 (C-11), 215.2 (C-2); MS, m/e 238 (M^+, 6), 223 (48), 153 (49), 125 (47), 95 (86), 93 (55), 83 (47), 81 (45), 79 (51), 71 (base), 69 (42), 67 (62), 55 (92), 53 (41).

Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.56; H, 11.00. Found: C, 75.60; H, 10.95.

Acknowledgment. L.M. and A.T. acknowledge gratefully support by the Consiglio Nazionale delle Ricerche and the Ministero della Pubblica Istruzione for the work in Perugia. We are indebted to Dr. R. Chadha for the X-ray analysis.

Registry No. **1**, 503-93-5; **2**, 108-31-6; **3**, 513-81-5; **4a**, 106-99-0; **4b**, 10034-09-0; (±)-**5**, 124562-44-3; (±)-**6**, 124562-45-4; (±)-**7a**, 124562-46-5; (±)-**7b**, 124562-50-1; (±)-**7c**, 124562-51-2; (±)-**8a**, 124562-47-6; (±)-**8b**, 124562-52-3; (±)-**9**, 124562-48-7; (±)-**10**, 124562-49-8.

Synthesis and Reactions of 7-Chloro-7-cyano-6b,7,8,8a-tetrahydrocyclobut[*a*]-acenaphthylene

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Received April 3, 1989

We have studied a variety of [2 + 2] cycloadditions to acenaphthylene (**1a**) using the heavy-atom solvent effect (HAE) to improve the yield through enhanced triplet excited-state formation of **1a**.[1,2] We discovered that 2-

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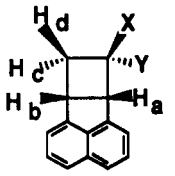
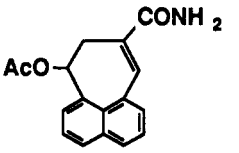
0022-3263/90/1955-1368$02.50/0

Chart I

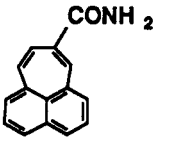
	1	2	3	4	5	6	7	8	9	10
X	Cl	CN	$CONH_2$	Cl	CO_2H	Cl	CN	H	$CONH_2$	H
Y	CN	Cl	Cl	$CONH_2$	Cl	CO_2H	H	CN	H	$CONH_2$



1-10

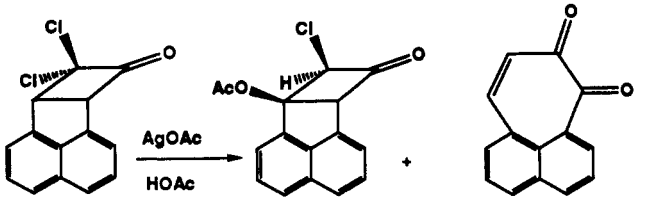


11



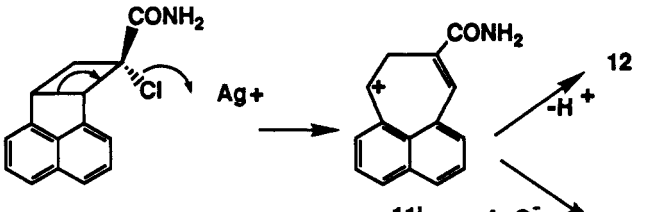
12

Scheme I



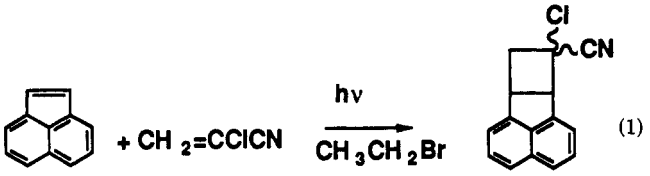
13 14 15

Scheme II



3 11l

chloroacrylonitrile is a more efficient trap for the excited triplet state of **1a** than is acrylonitrile. A 60% yield of an inseparable mixture of the (*E*)-7-chloro-7-cyanotetrahydrocyclobut[*a*]acenaphthylene (**1**, 44%) and the *Z* isomer (**2**, 56%) is produced upon irradiation of an excess of 2-chloroacrylonitrile in bromoethane while maintaining **1a** in a nitrogen-degassed, dilute concentration in the reaction mixture (eq 1).[3] This well-documented HAE is strong



(1)

1a **1 + 2**

support for the cycloaddition reaction occurring through the excited triplet of **1a**.[1-3] Because of 2-chloroacrylonitrile is very efficient as an excited triplet-state trapping agent, we intend to use it in studies of excited cycloaddition reactions of benzo-annelated acenaphthylenes.[4-9] Thus, we have explored the chemistry of the isomers **1** and **2** as a model system for the anticipated cycloadducts of annealated derivatives of **1a**.

The rearrangement with silver acetate[10] (Scheme I) of the cycloadduct (**13**), derived from the reaction of dichloro ketene and **1a** to produce **14** and **15** attracted our attention. The authors suggested that an intermediate carbocation was produced, which was captured by acetate to give **14** or rearranged to produce **15**. These results led us to treat mixtures of **1** and **2** with silver acetate in refluxing acetic acid to see if a similar fate would occur for **1** and **2**. From this reaction the hydrated chlorocarboxamides **3** and **4** were isolated along with the acetoxydihydropleiadiene **11** and the pleiadiene derivative **12**. On a large scale run **3** (Chart I) was selectively transformed into a mixture of **11** and **12**, while **4** was recovered unchanged. The mixture of **1** and **2** was refluxed with hydrochloric acid in acetic acid to see if selective hydration of one isomer would occur. With periodic monitoring, only trace amounts of amide were detected, even early in the run. Complete hydrolysis of **2** to the corresponding carboxylic acid (**5**) occurred, while **1** was barely affected within the same period of reflux. This fortuitous circumstance provided a method by which **1** could be separated from **2** through the selective transformation of **2** into **5**. Presumably, steric hindrance to acid-catalyzed hydrolysis to the more hindered syn nitrile group of **1** slows its hydrolysis rate.

To determine if either **1** or **2** were undergoing a rearrangement reaction promoted by silver acetate prior to the formation of **3** and **4**, mixtures of **1** and **2** were treated with silver acetate in refluxing acetic anhydride. After extended periods of time no detectable transformation was observed. The lack of reactivity of **1** and **2** under these conditions implies that products **11** and **12** are not formed directly from the nitriles **1** and **2**. We have shown that mercury(II) acetate in acetic acid promotes the hydration of nitriles and that silver acetate also is weakly active in this process.[11] Consequently, it appears that **1** and **2** are initially hydrated to a mixture of **3** and **4**. We propose that silver ion assisted ionization of **3** occurs with ring opening to form the intermediate carbocation (Scheme II). This pathway would avoid generation of significant positive charge at the α-carbon adjacent to the carbonyl group. In contrast, the isomers **1** and **2** do not rearrange under these conditions because silver ion assisted ionization of the chloride leaving group to form a carbocation is inhibited by the electronegativity of the nitrile group. Rearrangment of **3** probably occurs with greater facility because as the σ-orbital of the

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cyclobutane ring breaks, the bonding electron pair and associated orbital can move into a position for backside attack to generate the π-bond as chloride ion is lost.[12] A similar process in 4 probably has a higher activation energy due to the difficulty in rotating the bonds into the geometry required for support of the developing cationic charge as chloride is lost. Acetate-catalyzed proton elimination from 11i produces 12, while direct nucleophilic capture of the ion by acetic acid (or acetate) leads to the formation of 11. We hope to optimize this reaction to produce larger quantities of 12 because pleiadienes functionalized at the cycloheptadiene bridge are not readily available.[13-15]

We studied the reduction of 1 to see if selectivity in transformation to a single nitrile could be achieved. Reduction of 1 with zinc powder in refluxing acetic acid results in the quantitative formation of a mixture of the dechlorinated nitriles 7 and 8 in a ratio of 1:2.7, respectively, with the consequent loss of stereochemical integrity. Compounds 7 and 8 were separately hydrated with mercury(II) acetate in acetic acid to form the amides 9 and 10 for structural analysis.

The mixture of 1 and 2 was also treated under alkaline conditions to see if transformation into a single ketone[16,17] would occur. Treatment with hot DMSO and KOH produced a small quantity of 3 and 4 and intractable byproducts; similar results were obtained upon treatment of 1 and 2 with potassium *tert*-butoxide in hot *tert*-butyl alcohol. Other attempts[17] to produce the ketone were not successful.

The stereochemistry of the compounds was deduced by application of high-field NMR and COSY studies and by comparison with the previous analysis of the stereochemistry of comparable cycloadducts as reported by Hall[3] and Nakamura et al.[18] The NMR spectra of 3 and 4 produced the characteristic grouping of cyclobutyl protons between δ 3–5, a set of aromatic protons characteristic of acenaphthene, and amide proton resonances that were split into two separate broad peaks between δ 5 and 6.5.[19] These separated resonances were each representative of half of the proton count for the amide function. When 3 was dissolved into d_6-DMSO, the separated amide proton peaks could be made to coalesce near 85 °C. This phenomenon is widely recognized in studies of amide rotation.[20-22] These α-chloroamides are expected to have a substantial barrier to nitrogen rotation because the inductive effect of the chloro substituent enhances the resonance hybrid involving the nitrogen lone-pair delocalization. Compound 3 did not yield an accurate coalescence temperature because the amide resonances shifted into the aromatic region with increasing temperature and their coalecence could not be readily determined. The amide proton resonances of 4 in $CDCl_3$ occurred as two broad singlets at δ 6.32 and 5.32 and showed no significant

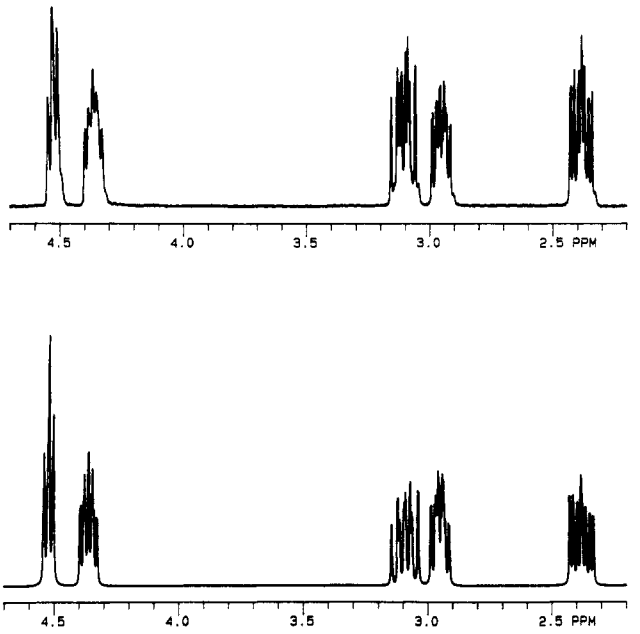

Figure 1. The 300-MHz NMR spectrum of (*E*)-7-cyano-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene ((*E*)-7, top) and its simulated spectrum (bottom) from use of the date in Table I (supplementary material).

chemical shift effect upon diluting the sample. The upfield shift of the amide protons in 4 compared to 3 is caused by the anisotropic shielding effect of the naphthalene ring and corroborates their geometry as being syn to the ring. We have reported[23] that the interesting reversal of the chemical shifts of H_c and H_d in the cyclobutyl region of 4 is attributable to a conformational preference for the carbonyl group over the aromatic rings.

The amide NMR resonances of 9 occurred at δ 5.53 and 5.37 in deuteriochloroform and coalesced to a single broad peak at δ 5.48 as the concentration of 9 was decreased by dilution. These results imply that monomeric 9 associated in concentrated chloroform solution to form equilibrium mixtures of hydrogen-bonded complexes that restrict the rotation of the NH_2 group, thus leading to two discrete proton environments. Interestingly, the chloroamides 3 and 4 do not exhibit this concentration-dependent behavior. The chloroamides exhibit hindered rotation even in dilute solution due to the enhanced resonance effect caused by the α-chloro substituent. Thus, no significant concentration-dependent change in the rotation of the amide function in 3 and 4 is expected.

The NMR spectrum of 11 also exhibits unique characteristics. We expected it to produce a typical AMX splitting pattern. However, the results obtained are quite different. The proton resonance H_a at δ 6.3 appears as a doublet; the geminal allylic proton H_b at δ 3.4 yields a doublet, and H_c at δ 2.9 produces a doublet of doublets. The olefinic proton at C7 (δ 7.7) is shifted into the aromatic region and the methyl of the acetoxy occurs at δ 2.1. The geometry of 11, as calculated by using the molecular mechanics program MMX,[24,25] is shown in I. The four-carbon bridge is relatively rigid and imposes severe geometric restrictions upon the bridge protons. The dihedral angle between H_a and H_b is computed to be 89°, while the di-

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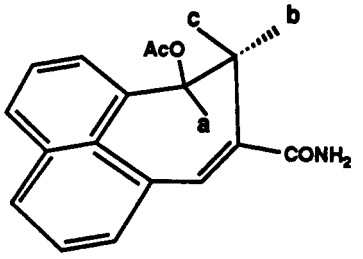

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hedral angle between H_a and H_c is 156°. The orthogonal relationship between H_a and H_b guarantees that these two protons will show minimum coupling; hence, the proton spectrum is simplified from that of a completely coupled AMX spectrum that is expected for a more flexible system. The resonance of H_c comes at the lowest field of the geminal pair because it is shielded by the adjacent aromatic ring. The magnitude of the coupling constants is also commensurate with the geometry and positions of the protons on the bridge: $J_{ab} \sim 0$ Hz, $J_{ac} = 7.9$ Hz, $J_{bc} = 16.2$ Hz. The double bond at C7–C8 is calculated to be rotated out of plane by 25°.

Experimental Section

General Methods. Melting points were taken on a Mel-Temp apparatus and are uncorrected. ^{1}H NMR spectra were obtained on either a Varian VXR-300 or EM-360 L spectrometer; chemical shifts are reported in δ with tetramethylsilane as the internal standard. Infrared spectra were recorded on a Perkin-Elmer 283 or on an IBM IR/32 FT spectrometer, and mass spectra were obtained with the Hewlett-Packard 5995 C GC/MS system operated at 70 eV. Photochemical syntheses were performed under nitrogen using a Hanovia 450-W mercury vapor lamp immersion-well apparatus with a uranium glass sleeve and circulating copper sulfate as a coolant and filter solution. Elemental analyses were performed by Galbraith or MicAnal.

Synthesis of (*E*)- and (*Z*)-7-Chloro-7-cyano-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene (1 and 2). A mixture of 1.0 g of acenaphthylene, 100 mL of freshly distilled 2-chloroacrylonitrile, and 380 mL of freshly distilled bromoethane was irradiated through a uranium glass filter with a water-cooled, 450 W Hanovia immersion lamp while continuously purging the solution with dry nitrogen gas beginning 15 min prior to the irradiation. When the solution bleached, an additional 1.0-g sample of acenaphthylene was added. By this procedure, up to 6.0 g of acenaphthylene could be added before polymer and photodimer formation interfered. The mixture was filtered to remove polymer and photodimer, and the filtrate was reduced by rotary evaporation to a viscous yellow–brown slurry. Column chromatography of the residue using a mixture of 10:1 cyclohexane:CH_2Cl_2 produced a middle fraction that contained an inseparable mixture of 1 and 2 in 60% yield. Anal. Calcd: C, 76.16; H, 4.21; Cl, 14.79; N, 5.86. Found: C, 75.38; H, 4.15; Cl, 14.82; N, 5.86 (analyzed as a mixture). ^{1}H NMR (300 MHz, $CDCl_3$): 1 δ 7.82 (d, 1 H), 7.75 (d, 1H), 7.62 (m, 2 H), 7.5 (dd, 1 H), 7.32 (d, 1 H), 4.94 (m, 1 H), 4.33 (m, 1 H), 3.62 (m, 1 H), 2.47 (m, 1 H); 2 δ 7.5 (m, 6 H, Ar H), 4.69 (m, 1 H), 4.51 (m, 1 H), 3.29 (m, 1 H), 2.83 (m, 1 H); mass spectra (70 eV), m/z (rel abundance) 239 (4), 204 (5), 176 (4), 152 (100), 88 (4), 75 (5); FTIR (KBr) 3053, 2952, 2230, 1611, 1493, 1424, 1365, 1024, 800 cm^{-1}.

(*Z*)-7-Carboxyl-7-chloro-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene (5). A mixture of 1 and 2 (1.0 g, 4.2 mmol) was dissolved in 25 mL of acetic acid containing 5.0 mL (6 M) of hydrochloric acid and heated at reflux for 24 h. The dark amber solution, when monitored by TLC, indicated the presence of unreacted starting material. The cooled solution was added to 125 mL of ice water and subsequently extracted with 3 × 50 mL portions of dichloromethane. The combined organic phase was washed with 2 × 25 mL of water, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The resulting dark oil was treated with 100 mL of a half-saturated solution of $NaHCO_3$ to produce a tan solid (0.25 g, mp 87–89 °C, crude 1). The clear aqueous phase was treated with charcoal and filtered, and the filtrate neutralized with excess concentrated HCl to produce an off-white precipitate (0.31 g, mp 153–163 °C). Dissolution of this crude acid in NaOH, followed by acid neutralization of the alkaline solution, and recrystallization of the crude acid from chloroform produced 0.2 g of 5, mp 163–165 °C; ^{1}H NMR ($CDCl_3$) δ 7.70 (d, 1 H), 7.65 (d, 1 H), 7.49 (d, 1 H), 7.43 (m, 1 H), 7.37 (m, 1 H), 7.28 (d, 1 H), 5.9 (br s, 1 H, disappeared upon addition of D_2O), 4.93 (m, 1 H), 4.20 (m, 1 H), 3.65 (m, 1 H), 2.39 (m, 1 H); FTIR (KBr) 3430, 3034, 2656, 1761, 1695, 1330, 796 cm^{-1}; mass spectrum (70 eV), m/z (rel abundance) 258 (4), 176 (9), 165 (4), 152 (100), 88 (5), 76 (5), 63 (4). Anal. Calcd: C, 69.64; H, 4.29; Cl, 13.70. Found: C, 69.29; H, 4.53; Cl, 13.80.

(*E*)-7-Carboxyl-7-chloro-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene (6). Compound 1 (0.10 g, 0.42 mmol) was dissolved in 6 mL of acetic acid containing 2.5 mL of concentrated HCl and refluxed for 48 h. The mixture was worked up as described for 5. The residue was recrystallized from $CHCl_3$:heptane with charcoal treatment to produce 0.05 g of 6, mp 178.5–179.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.78 (d, 1 H), 7.70 (d, 1 H), 7.6 (dd, 1 H), 7.50 (m, 2 H), 7.27 (d, 1 H), 6.0 (br s, 1 H), 4.67 (m, 1 H), 4.45 (m, 1 H), 3.02 (m, 1 H), 2.90 (m, 1 H). Anal. Calcd: C, 69.64; H, 4.29; Cl, 13.70. Found: C, 69.29; H, 4.03; Cl, 13.84.

Reaction of 1 and 2 with Silver Acetate. A mixture of 1 (44%) and 2 (56%) (1.0 g, 4.2 mmol) was dissolved in a mixture of 50 mL of acetic acid and silver acetate (0.84 g, 5 mmol) contained in a round-bottom flask with a reflux condenser and wrapped with foil to protect it from the light. After 24 h of reflux the dark amber solution indicated by TLC that all starting material had reacted. The warm solution was gravity filtered, and the filtrate poured into 150 mL of ice water. The aqueous milky-pink suspension was extracted with 3 × 50 mL portions of CH_2Cl_2 and the combined organic phase washed with 2 × 50 mL of water, dried over $MgSO_4$, and rotary evaporated to a dark red oil (1.32 g). The oil was chromatographed via radial chromatography using CH_2Cl_2 with 3% methanol as an eluate on a rotor containing 2 mm of silica gel. The following results were obtained (fraction, mass, %): (1, 0.18 g, 20) 1 and 2, (2, 0.33 g, 30) 4, (3, 0.22 g, 20) 3, (4, 0.02 g, 2.3) 12, and (5, 0.23 g, 19) 11. Analytical data: 4, mp 172.5–174.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, 1 H), 7.65 (d, 1 H), 7.48 (dd, 2 H), 7.33 (d, 1 H), 7.29 (d, 1 H), 5.32, 6.32 (br s, 2 H, NH_2), 4.67 (m, 1 H), 4.46 (m, 1 H), 3.13 (m, 1 H), 2.93 (m, 1 H); mass spectrum (70 eV), m/z (rel abundance) 257 (7), 207 (17), 178 (8), 152 (100), 88 (4), 75 (4), 63 (2); FTIR (KBr) 3467, 3289, 3154, 3055, 2956, 1689, 1609, 1380 cm^{-1}. Anal. Calcd: for 4: C, 69.91; H, 4.69; Cl, 13.76; N, 5.43. Found: C, 70.07; H, 4.45; Cl, 13.60; N 5.32. 3: mp 187.5–189.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, 1 H), 7.67 (d, 1 H), 7.57 (dd, 1 H), 7.48 (dd, 1 H), 7.38 (d, 1 H), 7.26 (d, 1 H), 6.65, 5.57 (br s, 2 H, NH_2), 4.88 (m, 1 H, cyclobutyl), 4.23 (m, 1 H, cyclobutyl), 3.58 (m, 1 H, cyclobutyl), 2.30 (m, 1 H, cyclobutyl); mass spectrum (70 eV), m/z (rel abundance) 257 (7), 207 (17), 178 (8), 152 (100), 88 (4), 75 (4), 63 (2); FTIR (KBr) 3467, 3289, 3154, 3055, 2956, 1689, 1609, 1380 cm^{-1}. Anal. Calcd: for 3: C, 69.91; H, 4.69; Cl, 13.76; N, 5.43. Found: C, 70.07; H, 4.54; Cl, 13.61; N 5.30. 12: mp 189–192 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3 (d, 1 H), 7.24 (d, 1 H), 7.03 (dd, 2 H), 6.8 (d, 1 H), 6.68 (d, 1 H), 6.73 (s, 1 H, vinyl) 6.09 (d, 1 H, J = 12.6 Hz, vinyl), 5.70 (d, 1 H, J = 12.6 Hz, vinyl), 5.61 (br s, 2 H, NH_2); FTIR (KBr) 3430, 3220, 1728, 1660, 1593, 1370, 1241 cm^{-1}; mass spectra (70 eV), m/z (rel abundance) 221 (100), 204 (11), 192 (6), 176 (70), 165 (43), 152 (21), 88 (25), 75 (12); exact mass calcd 222.139, found 222.135. 11: mp 159–161 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, 2 H) 7.68 (s, 1 H, vinyl H), 7.65 (d, 2 H), 7.52 (d, 2 H), 6.29 (d, 1 H), 6.05 (br s, 2 H, NH_2), 3.43 (dd, 1 H), 2.98 (d, 1 H), 2.04 (s, 3 H, CH_3); FTIR (KBr) 3377, 3199, 2962, 2924, 2853, 1653, 1639, 1596, 1102 cm^{-1}; mass spectra (70 eV), m/z (rel abundance) 281 (5), 221 (100), 204 (10), 193 (7), 176 (21), 165 (45), 152 (15), 88 (8). Anal. Calcd for 11: C, 72.58; H, 5,38; N, 4.98. Found: C, 72.53; H, 5.38; N, 4.76.

Zinc Dechlorination of 1. Compound 1 (0.025 g, 0.1 mmol) was dissolved in 50 mL of glacial acetic acid contained in a round-bottom flask equipped with magnetic stirrer, reflux condenser, and nitrogen inlet tube. To this stirred mixture was added previously prepared and dried Zn(Cu) couple (3.0 g). After 30

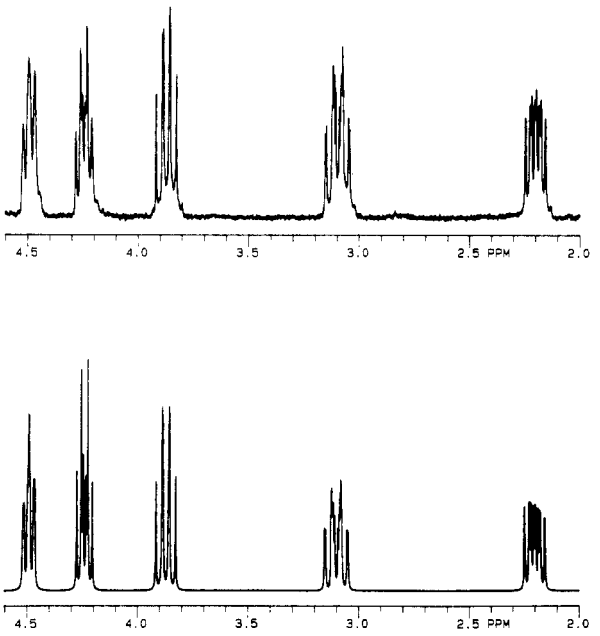

Figure 2. The 300-MHz NMR spectrum of (*Z*)-7-cyano-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene ((*Z*)-**8**, top) and its simulated spectrum (bottom) from use of the data in Table I (supplementary material).

min of reflux, the warm mixture was gravity filtered, and the filtrate poured into 100 mL of ice water. The aqueous solution was extracted with 2 × 50 mL of CH_2Cl_2, and the combined organic phase was washed with 50 mL of saturated $NaHCO_3$ and 50 mL of water and then dried over $MgSO_4$. Treatment of the organic phase with charcoal followed by rotary evaporation produced a pale yellow oil that slowly solidified. NMR analysis of the mixture indicated that by comparison with authentic samples[3] 27% of **7** and 73% of **8** were present in the mixture.

Synthesis of (*Z*)-7-Carboxamido-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene (10). A mixture of mercury(II) acetate (0.027 g, 0.085 mmol), 5.0 mL acetic acid, and **8** (0.035 g, 0.17 mmol) was refluxed for 25 h. The cooled reaction mixture was poured into ice water and extracted with 3 × 25 mL CH_2Cl_2, and the combined organic phases were washed with 3 × 25 mL of saturated $NaHCO_3$, dried over anhydrous $MgSO_4$, and rotary evaporated to a crude solid, 0.027 g, 71%. Recrystallization of the solid from $CHCl_3$:heptane produced **10**: mp 222.5–223.5 °C; IR (KBr) 3380, 3190, 1648, 1620, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.68 (d, 2 H), 7.50 (m, 2 H), 7.3 (dd, 2 H), 5.40 (br s, 2 H, NH_2), 4.43 (m, 1 H), 4.22 (m, 1 H), 3.05 (m, 1 H), 2.85 (m, 1 H), 2.3 (m, 1 H). Anal. Calcd: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.41; H, 5.90; N, 6.08. See Figures 1 and 2 for actual and simulated ^1H NMR spectra of (*E*)-**7** and (*Z*)-**8**.

Synthesis of (*E*)-7-Carboxamido-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene (9). This compound was prepared from **7**[3,18] as described for **10** in 65% yield, mp 179–180 °C; IR (KBr) 3380, 3190, 1650, 1620, 1591 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.68 (d, 1 H), 7.63 (d, 1 H), 7.48 (dd, 2 H), 7.37 (d, 1 H), 7.25 (d, 1 H), 5.17 (br s, 2 H, NH_2), 4.51 (m, 1 H), 4.18 (m, 1 H), 3.80 (q, 1 H), 2.85 (m, 1 H), 2.1 (m, 1 H). Anal. Calcd: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.60; H, 5.53; N, 6.16.

Acknowledgment. The support of the National Science Foundation through an NSF-RUI research grant is gratefully recognized. The partial support of the NSF and the Keck Foundation for the purchase of the VXR 300 NMR spectrometer is sincerely appreciated. We thank Dr. Susan T. Weintraub for obtaining a high-resolution mass spectrum.

Supplementary Material Available: ^1H NMR data for **1–10** (1 page). Ordering information is given on any current masthead page.

Kinetics of the Reaction between Carbon Dioxide and Tertiary Amines

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Received July 13, 1989

The reaction between carbon dioxide and amines is of great technical importance and has been the subject of many investigations.[1] We have shown that the reaction for secondary amines in anhydrous ethanol[2] and in aqueous solution[3] is exclusively second-order in amine and that the zwitterion intermediate postulated by Danckwerts[4] is probably of negligible significance in the mechanism. The reaction with tertiary amines has also been studied, but the data are less controversial. The product of the reaction is an alkylammonium hydrogen carbonate rather than the alkylammonium carbamate formed with a primary or secondary amine. Hydrogen carbonate ions are also formed by the direct reaction of carbon dioxide with water and with hydroxide ion, so that the following reactions occur in aqueous alkaline media. When an aqueous solution of carbon dioxide at its natural pH, around 4, is mixed with excess of an aqueous solution of a tertiary amine at its natural pH, around 9, hydrogen carbonate ions are formed at a rate given by:

$$CO_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+ + HCO_3^-$$

$$CO_2 + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HCO_3^-$$

$$R_3N + CO_2 + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} R_3NH^+ + HCO_3^-$$

$$d[HCO_3^-]/dt = k_1[H_2O][CO_2] + k_2[OH^-][CO_2] + k_3[R_3N][H_2O][CO_2] \quad (1)$$

Terms involving k_{-1}, k_{-2}, and k_{-3} are insignificant due to the magnitude of the various equilibrium and rate constants. Under these conditions, carbon dioxide is almost completely converted to hydrogen carbonate ion. Since $[R_3N] \gg [CO_2]$, we can rewrite eq 1 as:

$$d[HCO_3^-]/dt = k_o[CO_2] \quad (2)$$

where

$$k_o = k'_1 + k_2[OH^-] + k'_3[R_3N] \quad (3)$$

where the concentration of water has been included in the rate constants k'_1 and k'_3.

In order to complete our studies of the reactions of carbon dioxide with amines, using our conductimetric stopped-flow apparatus, we have studied this reaction for MDEA (methyldiethanolamine, IUPAC name *N*-methyl-2,2′-iminodiethanol) and TEA (triethanolamine, IUPAC name 2,2′,2″-nitrilotris(ethanol)). Our attempts to study this reaction with triethylamine and for quinuclidine failed. These amines are such strong bases (pK_a 10.75 and 10.95, respectively) that $[OH^-]$ is so large that $k_2[OH^-]$ dominates eq 2, and the contribution from the k_3 term is not seen.

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