A Novel Skeletal Rearrangement of 2-Azabicyclo[2.2.1]hept-5-ene-3-carboxylic Acid Derivatives into 2-Oxabicyclo[3.3.0]-oct-7-en-3-ones under Acidic Conditions

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The reaction of ethyl 2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate with aroyl chloride and the subsequent hydrolysis of the ester group provided 2-aroyl-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylic acid derivatives, which underwent a stereospecific rearrangement giving 4-aroylamino-2-oxabicyclo[3.3.0]oct-7-en-3-ones by treatment with trifluoroacetic acid. On the other hand, the reaction of 2-benzoyl-2-azabicyclo[2.2.1]hept-5-ene with trifluoroacetic acid in heated benzene afforded 1-[(benzoylamino)methyl]-1,3-cyclopentadiene which afforded a Diels–Alder cycloadduct with *N*-phenylmaleimide. A plausible mechanism for the rearrangement is presented.

The chemistry of systems derived from 2-azabicyclo[2.2.1]hept-5-ene has attracted a great deal of attention in the past years, due to its applicability to the syntheses of derivatives of biological and theoretical interest.[1] Although various methods of preparation of the 2-azabicyclo[2.2.1]hept-5-ene skeleton have been reported,[1,2] the Diels–Alder reaction of 1,3-cyclopentadiene with iminium ions in aqueous solution expedited the preparation of 2-azabicyclo[2.2.1]hept-5-enes with various substituents even in optically pure forms.[3,4] On the other hand, limited examples are known on the chemical properties of the skeleton, e.g., retro-Diels–Alder reactions,[5] N(2)–C(3) bond cleavage reactions,[1,3b] hetero [3,3] sigmatropic rearrangement reactions,[6] and rearrangement reactions via nitrenium intermediates.[7] We describe herein a novel type of acid-induced rearrangement of the 2-azabicyclo[2.2.1]-hept-5-ene-3-carboxylic acid derivatives into 2-oxabicyclo[3.3.0]oct-7-en-3-one skeleton.

Results and Discussion

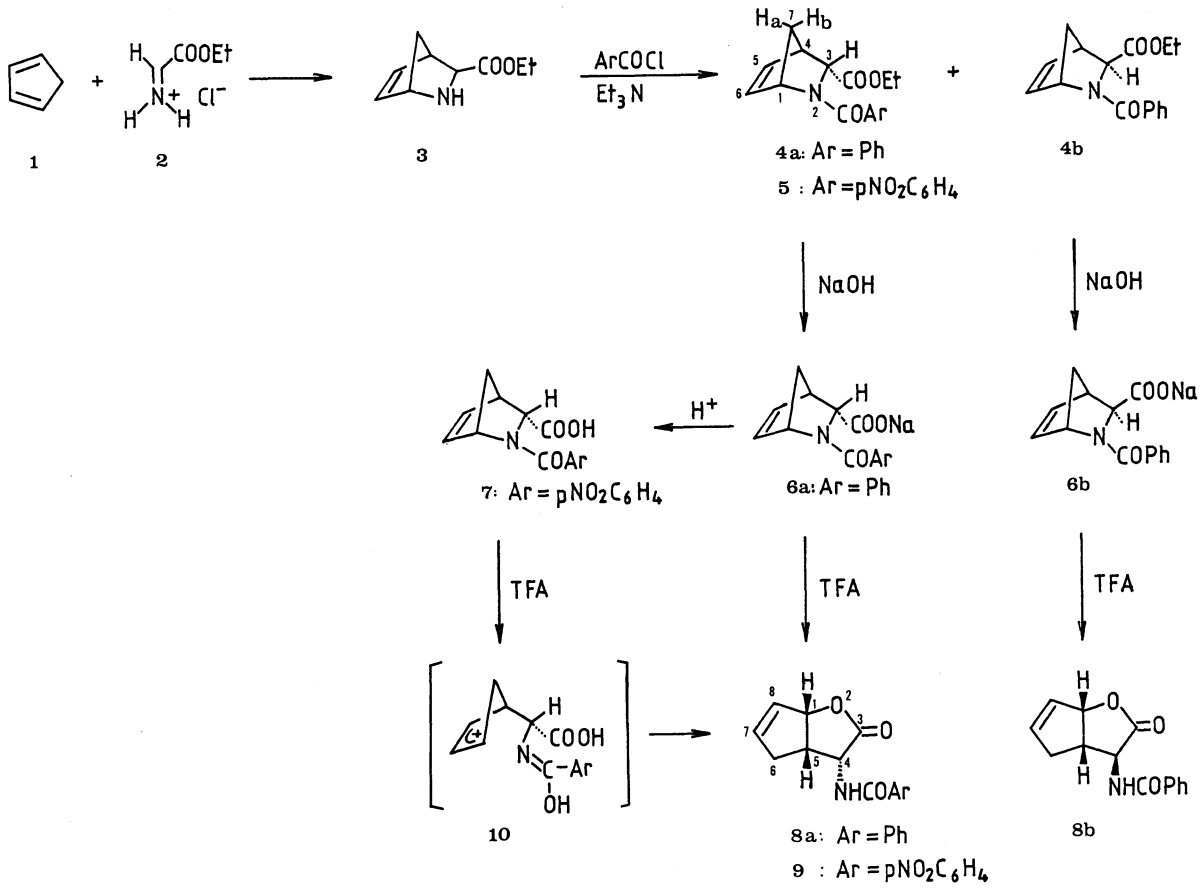
The aza-Diels–Alder reaction of 1,3-cyclopentadiene (**1**) with the iminium ion **2** in aqueous solution gave ethyl 2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate (**3**) in 84% yield.[3] The amino ester **3** was consequently treated with benzoyl chloride and triethylamine in dichloromethane at room temperature to give the 3-*endo*-ester amide **4a** and the 3-*exo*-ester amide **4b** in 57% and 20% yields, respectively. The reaction of the amine ester **3** with *p*-nitrobenzoyl chloride gave only the 3-*endo* isomer **5** in 48% yield.

The ester amides **4a**, **4b**, and **5** showed temperature-dependent NMR signals, which broadened at room temperature and sharpened at higher temperature, probably due to the restricted rotation around the N-COAr group.[8] The stereochemical determinations are based on ^{1}H NMR chemical shifts and vicinal ^{1}H coupling constants (δ=4.62, $J_{3,4}$=3.3 Hz for 3-H of **4a**; and δ=3.73, $J_{3,4}\approx$0 Hz for 3-H of **4b**). These assignments are further confirmed by the ^{1}H–^{1}H and ^{1}H–^{13}C COSY NMR measurements of **4a**. The *p*-nitrobenzoyl derivative **5** was determined to have a 3-*endo*-ethoxycarbonyl group by comparison of the spectra with those of the 3-*endo*-ester amide **4a**. These spectral properties are in good agreement with other 2-azabicyclo[2.2.1]hept-5-ene derivatives[9a] as well as norbornene systems.[9b]

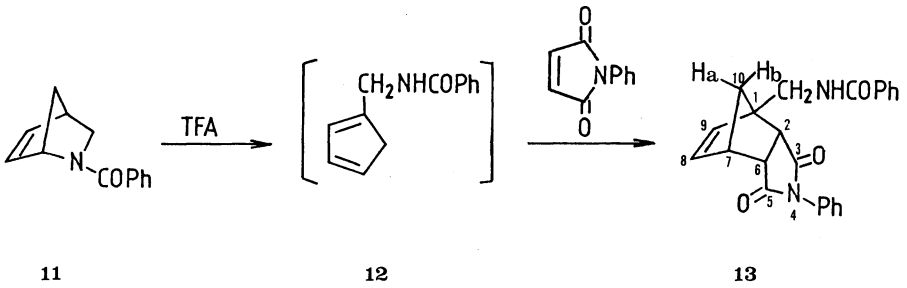
When the ester amide **4a** was hydrolyzed under alkaline conditions, the rearranged product subsequently identified as the lactone **8a** was obtained after acidification. Therefore, the ester amides **4a** and **4b** were converted respectively to the corresponding sodium carboxylates **6a** and **6b** in 86 and 59% yield without epimerization at the 3-position. The respective treatments of the 3-*endo* and the 3-*exo* carboxylates **6a** and **6b** with trifluoroacetic acid (TFA) resulted in the stereospecific formations of the 4-*endo* and the 4-*exo* lactones **8a** and **8b** in 86 and 60% yield. On the other hand, a similar hydrolysis of the *p*-nitrobenzoyl derivative **5** gave the 3-*endo* carboxylic acid **7** in 73% yield after acidification. Treatment of the acid **7** with TFA similarly afforded the 4-*endo* lactone **9** in 85% yield.

The structures of the lactones **8a**, **8b**, and **9** were unequivocally established by the spectroscopic and microanalytical data along with the ^{1}H–^{1}H and ^{1}H–^{13}C COSY spectra of **8a**. Comparison of the ^{1}H NMR spectra between the lactones **8a** and **8b** revealed a characteristic upfield shift by 0.65 ppm of 4-H for the 4-*exo* lactone **8b**, attributable to the shielding effect by the olefin moiety. The vicinal coupling constants between the 4-H and 5-H protons showed a large coupling constant ($J_{4,5}$=9.2 Hz) in the case of the 4-*endo* lactone **8a** and a medium coupling constant ($J_{4,5}$=7.7 Hz) in the case of the 4-*exo* lactone **8b**. The ^{1}H NMR data of the 4-*exo* lactone **8b** agree with those of the same skeleton previously reported.[10]

On the other hand, the reaction of 2-benzoyl-2-azabicyclo[2.2.1]hept-5-ene (**11**) with TFA as solvent at room temperature resulted in the formation of a complex mixture. However, the treatment of the amide **11** with a catalytic amount of TFA in refluxing benzene provided labile crystals which were tentatively identified as 1-[(benzoylamino)methyl]-1,3-cyclopentadiene (**12**). A



Scheme 1.



Scheme 2.

similar reaction of **11** in the presence of *N*-phenylmaleimide afforded the cycloadduct **13** in 45% yield.

Based on the results presented above, the formation of the lactones **8a**, **8b**, and **9** is explainable by an acid-induced cleavage of the C(1)–N(2) bond of **6a**, **6b**, and **7** giving allyl cationic intermediates such as **10** and their subsequent cyclization to the lactones as shown for the *p*-nitrobenzoyl drivative in Scheme 1. Although an alternative route involving hetero [3,3] sigmatropic rearrangement[6,10,11] cannot be excluded, the stereospecificity observed in this rearrangement cannot reconcile to a route via retro-Diels–Alder fragmentation.[12–14]

In summary, the reactions described above offer a novel type of the acid-induced reactions of the 2-azabicyclo[2.2.1]hept-5-enes, which have been reported to undergo the retro-Diels–Alder reaction under acidic conditions.[5,12] The products of the rearrangement reactions, 2-oxabicyclo[3.3.0]oct-7-en-3-ones, could be potentially useful for the syntheses of biologically active molecules.[15]

Experimental

General. All the melting points were recorded with a Yanagimoto hot-stage apparatus and uncorrected. The IR spectra were obtained with a Hitachi 345 spectrometer. The ^1H (90 MHz) and ^{13}C NMR (22.5 MHz) spectra were recorded with a JEOL-FX-90Q spectrometer with tetramethylsilane as an internal standard. The mass spectra were taken with a

Shimadzu GCMS-QP1000 and a JEOL 01SG spectrometers. Elemental analyses were performed with a Perkin-Elmer Model 240 apparatus.

Ethyl 2-Benzoyl-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate (4a, 4b): A solution of 1,3-cyclopentadiene (7.58 g, 115 mmol) and ethyl glyoxylate[16] (5.50 g, 54 mmol) in saturated aq NH_4Cl (26 ml) was stirred for 7 h at room temperature under nitrogen. The mixture was washed with ether and the pH of the aqueous phase was brought to 9 with $NaHCO_3$. The product was extracted with $CHCl_3$ prior to drying over Na_2SO_4. Removal of the solvent in vacuo gave ethyl 2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate (**3**) as a yellow oil (7.59 g, 84%): IR (neat) 3329 (NH), 1733 (C=O)cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.25 (2.25H, t, J=7.0 Hz, *endo* CH_3), 1.29 (0.75H, t, J=6.9 Hz, *exo* CH_3), 1.30—1.75 (2H, m, 7-H), 2.67 (1H, br, NH), 2.94 (0.25H, br s, *exo* 3-H), 3.25 (0.25H, br s, *exo* 4-H), 3.45 (0.75H, br s, *endo* 4-H), 3.92 (0.75H, d, J=3.1 Hz, *endo* 3-H), 3.94—4.40 (3H, m, CH_2 and 1-H), 5.80—6.05 (1H, m, 5-H), 6.21—6.40 (1H, m, 6-H); MS m/z (rel intensity) 167 (M^+, 2), 121 (3), 102 (16), 94 (43), 66 (100). Attempted distillation of the amino ester **3** gave a red tarry material and conversion of **3** into the hydrochloride or oxalate was unsuccessful.

Benzoyl chloride (5.91 g, 42 mmol) was added to a solution of the amino ester **3** (7.59 g) and triethylamine (5.05 g, 50 mmol) in CH_2Cl_2 (30 ml), and the mixture was stirred at room temperature for 20 h. The mixture was washed with aq $NaHCO_3$, dried over Na_2SO_4, and concentrated. The residue was separated with a Lobar column (silica gel, hexane–ethyl acetate=1/1) to provide the 3-*endo*-ester amide **4a** (8.33 g, 57%) and the 3-*exo*-ester amide **4b** (2.99 g, 20%). The yields are based on the amount of ethyl glyoxylate.

4a: Colorless oil; IR (neat) 1753 (COOEt), 1629 (NCOPh) cm^{-1}; ^{1}H NMR ($(CD_3)_2SO$, 100 °C) δ=1.11 (3H, t, J=7.1 Hz, CH_3), 1.63 (1H, dt, J=8.6, 1.6 Hz, 7-H_b), 1.72 (1H, dt, J=8.6, 1.6 Hz, 7-H_a), 3.49 (1H, m, 4-H), 4.00 (2H, q, J=7.1 Hz, CH_2), 4.62 (1H, d, J=3.3 Hz, 3-H), 4.64 (1H, br s, 1-H), 6.17 (1H, dd, J=5.8, 2.6 Hz, 5-H), 6.57 (1H, dd, J=5.8, 2.6 Hz, 6-H), 7.44 (5H, br s, Ph); ^{13}C NMR ($(CD_3)_2SO$, 80 °C) δ=13.3 (q, CH_3), 46.7 (d, C-4), 48.9 (t, C-7), 57.4 (d, C-1), 59.6 (t, CH_2), 63.6 (d, C-3), 126.6 (d), 127.5 (d), 129.3 (d), 134.6 (d, C-5), 135.1 (s), 136.3 (d, C-6), 167.0, 168.4; MS m/z (rel intensity) 271 (M^+, 6), 225 (40), 198 (17), 166 (79), 105 (100), 92 (21). Found: C, 71.21; H, 6.57; N, 4.93%. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16%.

4b: Colorless oil; IR (neat) 1752 (COOEt), 1639 (NCOPh) cm^{-1}; ^{1}H NMR ($(CD_3)_2SO$, 100 °C) δ=1.24 (3H, t, J=7.1 Hz, CH_3), 1.52 (1H, d, J=8.9 Hz, 7-H_b), 2.13 (1H, d, J=8.9 Hz, 7-H_a), 3.37 (1H, br s, 4-H), 3.73 (1H, s, 3-H), 4.17 (2H, q, J=7.1 Hz, CH_2), 4.75 (1H, br s, 1-H), 6.48 (2H, m, 5,6-H), 7.45 (5H, br s, Ph); ^{13}C NMR ($(CD_3)_2SO$, 80 °C) δ=13.3 (q, CH_3), 44.6 (t, C-7), 47.3 (d, C-4), 58.0 (d, C-1), 60.1 (t, CH_2), 62.4 (d, C-3), 126.2 (d), 127.7 (d), 129.2 (d), 135.6 (d, C-5), 136.1 (s), 137.4 (d, C-6), 168.4, 169.7; MS m/z (rel intensity) 271 (M^+, 9), 206 (15), 198 (50), 166 (6), 105 (100), 65 (9). Found: C, 71.16; H, 6.59; N, 4.78%. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16%.

Ethyl 2-(*p*-Nitrobenzoyl)-2-azabicyclo[2.2.1]hept-5-ene-3-*endo*-carboxylate (5): According to a similar procedure as described for **4**, the amino ester **3** (2.82 g, 17 mmol) was treated with *p*-nitrobenzoyl chloride (3.12 g, 17 mmol) and triethylamine (1.98 g, 18 mmol) in CH_2Cl_2 (20 ml) to give the 3-*endo* isomer **5** (2.60 g, 48%) after recrystallization from ethanol: Mp 122—123 °C; IR (KBr) 1759 (COOEt), 1634 (NCOAr) cm^{-1}; ^{1}H NMR ($(CD_3)_2SO$, 100 °C) δ=1.11 (3H, t, J=7.0 Hz, CH_3), 1.65 (1H, d, J=8.3 Hz, 7-H_b), 1.80 (1H, d, J=8.3 Hz, 7-H_a), 3.55 (1H, br s, 4-H), 3.98 (2H, q, J=7.0 Hz, CH_2), 4.66 (1H, d, J=3.3 Hz, 3-H), 4.68 (1H, m, 1-H), 6.08—6.30 (1H, m, 5-H), 6.44—6.68 (1H, m, 6-H), 7.71 (2H, d, J=8.9 Hz), 8.25 (2H, d, J=8.9 Hz); ^{13}C NMR ($(CD_3)_2SO$, 80 °C) δ=13.3 (CH_3), 46.8 (C-4), 48.9 (C-7), 57.4 (C-1), 59.9 (CH_2), 63.7 (C-3), 122.9, 128.0, 134.8 (C-5), 135.0 (C-6), 142.2, 148.0, 165.0, 168.2; MS m/z (rel intensity) 316 (M^+, 7), 243 (47), 150 (83), 104 (100), 92 (99), 66 (28). Found: C, 60.75; H, 4.82; N, 8.85%. Calcd for $C_{16}H_{16}N_2O_5$: C, 60.76; H, 5.10; N, 8.86%.

4-*endo*-Benzoylamino-2-oxabicyclo[3.3.0]oct-7-en-3-one (8a): A solution of the ester amide **4a** (5.92 g, 22 mmol) and NaOH (0.88 g, 22 mmol) in a mixture of ethanol and water (15 ml, 2:1) was stirred at room temperature for 24 h. The mixture was concentrated and water (30 ml) was added into the residue. The aqueous solution was washed with benzene (10 ml×2) and concentrated to give the sodium 3-*endo*-carboxylate **6a** (4.97 g, 86%) as colorless plates: Mp 168 °C (decomp); IR (KBr) 1645 (NC=O), 1600 (COO^-) cm^{-1}; ^{1}H NMR ($(CD_3)_2SO$, 100 °C) δ=1.52 (2H, br s, 7-H), 3.44 (1H, br s, 4-H), 4.32 (1H, d, J=3.3 Hz, 3-H), 4.53 (1H, br s, 1-H), 6.14—6.30 (1H, m, 5-H), 6.31—6.49 (1H, m, 6-H), 7.20—7.60 (5H, m, Ph). Found: C, 62.70; H, 4.63; N, 5.10%. Calcd for $C_{14}H_{12}NO_3Na$: C, 63.40; H, 4.56; N, 5.28%. The sodium carboxylate **6a** was almost pure and used without further purification.

A solution of the sodium carboxylate **6a** (1.30 g, 4.9 mmol) in trifluoroacetic acid (TFA, 2 ml) was stirred at room temperature for 6 h. The solution was concentrated and the residue was dissolved in $CHCl_3$, which was successively washed with aq $NaHCO_3$ and water, and dried over Na_2SO_4. Removal of the solvent afforded **8a** (1.04 g, 87%) as colorless prisms: Mp 172—173 °C (benzene); IR (KBr) 3266 (NH), 1770 (O-C=O), 1643 (N-C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.34—2.57 (2H, m, 6-H), 3.61 (1H, m, 5-H), 5.40 (1H, dd, J=9.2, 5.5 Hz, 4-H), 5.44 (1H, m, 1-H), 5.83—6.03 (1H, m, 8-H), 6.09—6.39 (1H, m, 7-H), 7.07—7.24 (1H, br, NH), 7.31—7.60 (3H, m), 7.70—7.94 (2H, m); ^{13}C NMR ($CDCl_3$) δ=32.1 (t, C-6), 40.4 (d, C-5), 52.8 (d, C-4), 87.3 (d, C-1), 127.3 (d), 127.7 (d, C-8), 128.5 (d), 131.9 (d) 133.0 (s), 140.6 (d, C-7), 167.8 (s), 175.0 (s); MS m/z (rel intensity) 243 (M^+, 1), 199 (15, M^+-CO_2), 121 (40), 105 (100), 78 (17). Found: C, 69.05; H, 5.27; N, 5.70%. Calcd for $C_{14}H_{13}NO_3$: C, 69.12, H, 5.39; N, 5.76%.

4-*exo*-Benzoylamino-2-oxabicyclo[3.3.0]oct-7-en-3-one (8b): By a similar procedure as described for **8a**, the ester amide **4b** (1.35 g, 5 mmol) was treated with NaOH (0.20 g, 5 mmol) in a mixture of ethanol and water (6 ml, 2:1) to give the sodium 3-*exo* carboxylate **6b** (0.78 g, 59%) as colorless plates: Mp 170 °C (decomp); IR (KBr) 1642 (N-C=O), 1597 (COO^-) cm^{-1}; ^{1}H NMR ($(CD_3)_2SO$, 100 °C) δ=1.30 (1H, d, J=8.0 Hz, 7-H_b), 2.28 (1H, d, J=8.0 Hz, 7-H_a), 3.28 (1H, br s, 4-H), 3.33 (1H, s, 3-H), 4.65 (1H, br s, 1-H), 6.36 (2H, m, 5,6-H), 7.22—7.60 (5H, m, Ph). Found: C, 62.53; H, 4.65; N, 5.10%. Calcd for $C_{14}H_{12}NO_3Na$: C, 63.40; H, 4.56, N, 5.28%. The sodium carboxylate **6b** was almost pure and used without further purification.

The reaction of **6b** (200 mg, 0.75 mmol) with TFA (1 ml) provided the 4-*exo* lactone **8b** (109 mg, 60%) as colorless prisms: Mp 182—183 °C (benzene); IR (KBr) 3329 (NH), 1783 (O-C=O), 1648 (N-C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.69—

2.91 (2H, m, 6-H), 3.00—3.35 (1H, m, 5-H), 4.39 (1H, dd, J=7.7, 6.7 Hz, 4-H), 5.64 (1H, m, 1-H), 5.80—6.00 (1H, m, 8-H), 6.04—6.21 (1H, m, 7-H), 7.00—7.20 (1H, m, NH), 7.29—7.60 (3H, m), 7.62—7.89 (2H, m); ^{13}C NMR ($CDCl_3$) δ=37.3 (t, C-6), 41.7 (d, C-5), 56.1 (d, C-4), 86.9 (d, C-1), 127.4 (d), 128.5 (d), 129.2 (d, C-8), 131.8 (d), 133.1 (s), 136.7 (d, C-7), 165.9 (s), 174.6 (s); MS m/z (rel intensity) 199 (M^+-CO_2, 19), 138 (11), 121 (40), 105 (100), 78 (19). Found: C, 69.49; H, 5.46; N, 5.88%. Calcd for $C_{14}H_{13}NO_3$: C, 69.13, H, 5.39; N, 5.76%.

2-(*p*-Nitrobenzoyl)-2-azabicyclo[2.2.1]hept-5-ene-3-*endo*-carboxylic Acid (7): A solution of the ester amide **5** (316 mg, 1.0 mmol) and 5%-aq NaOH (2 ml) in ethanol (20 ml) was stirred at 40 °C for 24 h. After removal of ethanol in vacuo, water was added to the residue and the solution was acidified with 5%-aq HCl. The resulted solid was filtered and washed with water to give the carboxylic acid **7** (210 mg, 73%): Mp 168—169 °C (CH_3CN); IR (KBr) 3441 (OH), 1764 (COOH), 1616 (N-C=O) cm^{-1}; ^{1}H NMR (($CD_3)_2SO$, 100 °C) δ=1.64 (1H, d, J=8.3 Hz, 7-H_b), 1.81 (1H, d, J=8.3 Hz, 7-H_a), 3.69 (1H, br s, 4-H), 4.76 (1H, d, J=3.3 Hz, 3-H), 4.78 (1H, br s, 1-H), 6.53 (2H, m, 5,6-H), 7.70 (2H, d, J=8.7 Hz), 8.31 (2H, d, J=8.7 Hz); ^{13}C NMR (($CD_3)_2SO$, 100 °C) δ=45.9 (d, C-4), 49.0 (t, C-7), 57.5 (d, C-1), 63.7 (d, C-3), 123.0 (d), 128.2 (d), 135.0 (d, C-5), 135.2 (d, C-6), 142.5 (s), 148.1 (s), 165.3 (s), 169.6 (s); MS m/z (rel intensity) 288 (M^+, 2), 270 (38), 244 (100), 150 (90), 104 (50), 77 (82). Found: C, 58.61; H, 4.27; N, 10.02%. Calcd for $C_{14}H_{12}N_2O_5$: C, 58.33; H, 4.20; N, 9.72%.

4-*endo*-(*p*-Nitrobenzoylamino)-2-oxabicyclo[3.3.0]oct-7-en-3-one (9): By a similar procedure as described for **8a**, the acid **7** (288 mg, 1.0 mmol) was stirred in TFA (1 ml) for 25 min to give **9** (244 mg, 85%) as colorless needles: Mp 222 °C (decomp, $CHCl_3$); IR (KBr) 3291 (NH), 1770 (O-C=O), 1643 (N-C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.40—2.60 (2H, m, 6-H), 3.66 (1H, m, 5-H), 5.00 (1H, dd, J=9.3, 4.7 Hz, 4-H), 5.42—5.60 (1H, m, 1-H), 6.02 (1H, m, 8-H), 6.25 (1H, m, 7-H), 7.01 (1H, br, NH), 8.02 (2H, d, J=9.0 Hz), 8.31 (2H, d, J=9.0 Hz); ^{13}C NMR ($CDCl_3$) δ=31.9 (C-6), 39.2 (C-5), 51.3 (C-4), 86.3 (C-1), 123.4, 127.6 (C-8), 128.8, 138.9, 140.7 (C-7), 149.1, 164.9, 174.0; MS m/z (rel intensity) 244 (M^+-CO_2, 20), 150 (100), 104 (14), 66 (53). Found: C, 58.65; H, 4.13; N, 9.50%. Calcd for $C_{14}H_{12}N_2O_5$: C, 58.33; H, 4.20; N, 9.72%.

2-Benzoyl-2-azabicyclo[2.2.1]hept-5-ene (11): A mixture of 1,3-cyclopentadiene (6.60 g, 0.1 mol) and 35% formalin (4.30 g, 0.05 mmol) in saturated aq NH_4Cl (20 ml) was stirred for 18 h at room temperature.[3a] The mixture was washed with ether and the aqueous layer was concentrated. To the residue were added benzoyl chloride (7.03 g, 0.05 mol) and 33% aq NaOH (37 ml, 120 mmol), and the mixture was stirred for 17 h at room temperature. The product was extracted with CH_2Cl_2, and the organic phase was dried over Na_2SO_4 and concentrated. Purification by column chromatography (silica gel, hexane/ethyl acetate=1/1) gave **11** (3.34 g, 34% based on formalin) as colorless prisms: Mp 71—72 °C (hexane-Et_2O); IR (KBr) 1622 (C=O) cm^{-1}; ^{1}H NMR (($CD_3)_2SO$, 100 °C) δ=1.44—1.74 (2H, m, 7-H), 2.67 (1H, d, J=9.8 Hz, 3-H_{endo}), 3.26 (1H, br s, 4-H), 3.74 (1H, dd, J=9.8, 3.0 Hz, 3-H_{exo}), 4.69 (1H, br s, 1-H), 6.36 (2H, br s, 5,6-H), 7.44 (5H, br s, Ph); ^{13}C NMR (($CD_3)_2SO$, 100 °C) δ=42.2, 46.4, 47.3, 61.2, 126.5, 127.5, 128.5, 129.0, 133.4, 136.8, 168.4; MS m/z (rel intensity) 199 (M^+, 45), 134 (49), 105 (100), 77 (90), 65 (74). Found: C, 78.28; H, 6.66; N, 6.88%. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03%.

The Reaction of 11 with Trifluoroacetic Acid. A solution of **11** (200 mg, 1.0 mmol) and TFA (11 mg, 0.1 mmol) in anhydrous benzene (12 ml) was refluxed for 17 h. Removal of the solvent and trituration of the residue with Et_2O afforded white powders which were tentatively assigned as 1-[(benzoylamino)methyl]-1,3-cyclopentadiene (**12**) (47 mg, 24%): Mp 93—95 °C; IR (KBr) 3325 (NH), 1646 (N-C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.01 (2H, d, J=0.9 Hz, N-CH_2), 4.32—4.50 (2H, m, 5-H), 6.17—6.60 (4H, m), 7.31—7.58 (3H, m), 7.70—7.89 (2H, m); MS m/z (rel intensity) 199 (M^+, 18), 105 (100), 77 (97), 65 (15).

A similar reaction of **11** (200 mg, 1.0 mmol) in the presence of *N*-phenylmaleimide (173 mg, 1.0 mmol) gave the cycloadduct **13** (174 mg, 47%): Mp 169—170 °C (ethyl acetate); IR (KBr) 3401 (NH), 1702 (C=O), 1640 (N-CO-Ph) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.71 (1H, d, J=8.7 Hz, 10-H_b), 1.81 (1H, d, J=8.7 Hz, 10-H_a), 3.41 (1H, d, J=7.4 Hz, 2-H), 3.45—3.59 (3H, m, 6-H, 7-H, and CH-NHCO), 4.32 (1H, dd, J=14.2, 7.7 Hz, CH-NHCO), 6.26 (2H, br s, 8-H and 9-H), 7.00—7.55 (8H, m), 7.80—8.00 (2H, m), 8.13 (1H, br, NH); ^{13}C NMR ($CDCl_3$) δ=42.4 (t), 45.2 (d), 48.0 (d), 49.8 (d), 55.8 (t), 57.9 (s), 126.7, 127.2, 128.5, 128.8, 129.1, 131.4, 131.7, 134.2, 135.1, 135.6, 167.6 (s), 176.0 (s), 177.9 (s); MS m/z (rel intensity) 372 (M^+, 9), 239 (15), 199 (18), 105 (100). Found: C, 74.24; H, 5.23; N, 7.36%. Calcd for $C_{23}H_{20}N_2O_3$: C, 74.18; H, 5.41; N, 7.52%.

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