Reaction of Bicyclic Enamines with Aryl Azides

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There are a number of reports in the literature dealing with the reactions of acyclic and alicyclic enamines with aromatic azides (1-5). We made a brief study of the reactions of selected bicyclic enamines with various phenyl azides and with benzoyl azide.

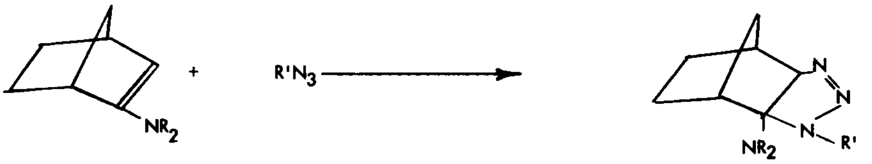
2-*N*-Morpholinobicyclo[2.2.1]hept-2-ene (Ia) (6-7) reacted readily with phenyl azide (IIa) to afford a cyclo-addition product which was assigned structure IIIa on the basis of elemental analysis and by analogy with the work of Munk and Kim (5). These authors have demonstrated that triazolines formed by cyclo-addition of phenyl azide with enamines are the products of electronic control: the negative end of the azide dipole, that is, the nitrogen atom bearing the phenyl group is directed to the carbon of the enamine double bond bearing the amino group. Under similar conditions, Ia reacted with IIb and IIc to furnish the corresponding triazoline derivatives IIIb and IIIc (see Chart I).

Although both *exo* and *endo* additions to Ia are possible, it is to be anticipated that *endo* addition will be less favored for steric reasons (8). The NMR spectra of adducts IIIa, IIIb and IIIc offer direct confirmation of *exo* addition. It is well known in the case of norbornane derivatives that an *exo* proton (H-3a in IIIa), but not an *endo* proton, will couple with the bridgehead proton (H-4 in IIIa) (9,10). This phenomenon is caused by the different dihedral angles between the C-H bonds involved and the well-known dependence of coupling constants on dihedral angle (11,12). The dihedral angle between C-H (*endo*) and C-H (bridgehead) is 82° (13,14), and in keeping with the Karplus predictions there is no coupling between these protons. The dihedral angle between C-H (*exo*) and C-H (bridgehead) is 42° and coupling constants of 3-5 Hz have been observed (15). In the NMR spectra of the triazolines IIIa, IIIb and IIIc the signal due to the 3a-proton appears in each case as a singlet, indicating that the heterocyclic ring in IIIa, IIIb and IIIc is in the *exo* configuration.

When benzoyl azide (IV) was allowed to react with Ia, the triazoline Va was formed. With 2-*N*-pyrrolidinobicyclo[2.2.1]hept-2-ene (Ib) and 2-*N*-piperidinobicyclo-[2.2.1]hept-2-ene (Ic), benzoyl azide gave the corresponding triazoline adducts Vb and Vc (see Chart II). In contrast to the related 1-benzoyl-4,7-methano-3a,4,5,6,7,7a-hexahydrobenzotriazole (the amino group in Va-Vc is replaced by hydrogen), which has been observed only in solution and which decomposes in solution at 40° (14), the aminotriazolines Va, Vb and Vc are well-defined crystalline compounds. The NMR spectra of the triazolines Va, Vb and Vc were similar to those of the phenyl-substituted aminotriazolines described above, and each showed the 3a-proton signal as a singlet, indicating that the heterocyclic ring in Va, Vb and Vc is in the *exo* configuration.

During work-up, which involved recrystallization from hot methanol, triazoline Vb was partially converted into

CHART I



Ia, $-NR_2$ = morphilino

IIa, R' = C_6H_5

IIb, R' = $(4)Cl-C_6H_4$

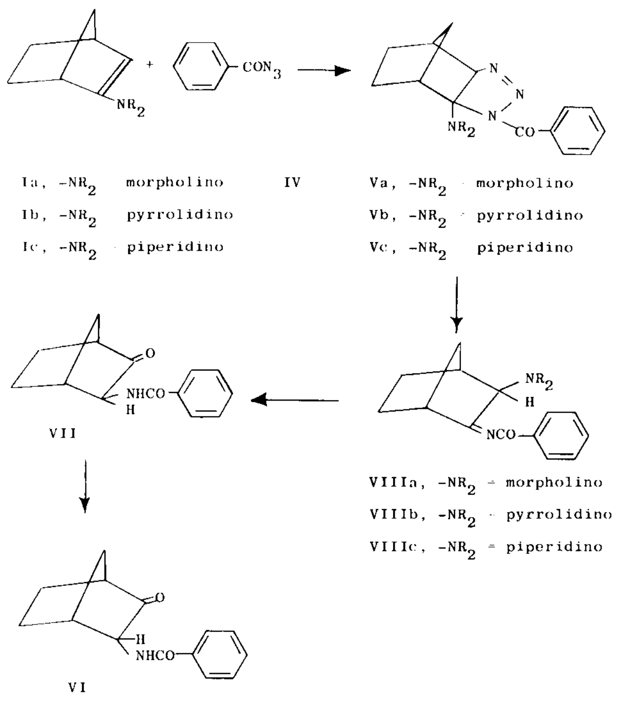
IIc, R' = $(4)NO_2-C_6H_4$

IIIa, $-NR_2$ = morpholino; R' = C_6H_5

IIIb, $-NR_2$ = morpholino; R' = $(4)Cl-C_6H_4$

IIIc, $-NR_2$ = morpholino; R' = $(4)NO_2-C_6H_4$

CHART II



a compound $C_{14}H_{15}NO_2$ which was formulated as *endo*-3-benzamidonorbornanone (VI) on the basis of spectral data (16). The infrared spectrum of VI showed N-H absorption at 3.01 μ, carbonyl absorption at 5.71 μ attributable to the norbornanone carbonyl, and a peak at 6.12 μ attributable to the secondary amide carbonyl. The 100-MHz NMR spectrum of VI in deuteriochloroform exhibited signals in the ratio of 2:3:1:1:1:1:6 in the direction of stronger field. Multiplets at δ 7.91-7.70 and δ 7.58-7.25 were assigned to the five aromatic hydrogens. A broad signal at δ 6.98-6.72 was assigned to the hydrogen attached to nitrogen, and a triplet centered at δ 4.32 ($J_{3,4}$ = 5 Hz) was attributed to the 3-*exo* hydrogen. The magnitude of the coupling constant clearly establishes the *exo* configuration of this hydrogen (15). Broad peaks at δ 3.23-3.05 and δ 2.80-2.64 were observed for the C_4 and C_1 bridgehead hydrogens, respectively. A complex multiplet between δ 2.15 and δ 1.28 was assigned to the six C_5, C_6 and C_7 hydrogens.

Triazoline Vc was also partially decomposed during recrystallization from hot methanol to afford a compound VII, which was isomeric with VI. The structure of VII was based on spectral evidence. Significantly, the infrared spectrum of this compound displayed absorption at 3.08 μ due to the N-H function; bands at 5.72 and 6.13 μ were assigned to the norbornanone and secondary amide carbonyl groups, respectively. The 100-MHz NMR spectrum of VII in DMF-d_6 showed signals in the ratio of 1:5:1:2:1:5 in the direction of stronger field. The absorption for the hydrogen attached to nitrogen appeared as a doublet at δ 8.56 ($J_{3,NH}$ = 7.0 Hz). Multiplets at δ 8.09-7.83 and δ 7.65-7.26 were readily assigned to the five aromatic hydrogens. A quartet centered at δ 4.04 ($J_{3,7}$ *anti* = 3.5 Hz, $J_{3,NH}$ = 7.0 Hz) was attributed to the 3-*endo* hydrogen. The magnitude of the coupling constant together with the observation that this hydrogen appears at higher field than in its epimer VI, which appears at δ 4.53 in DMF-d_6 (δ 4.32 in deuteriochloroform), demonstrate that this compound must be *exo*-3-benzamidonorbornanone (VII). Many studies have shown that *exo* protons occur at lower field than do *endo* protons for epimers in the norbornane series (17). A broad signal at δ 2.61-2.46 was assigned to the two bridgehead hydrogens. The C_7 bridge methylene signals appeared as an AB-type quartet. The two peaks of the lower field doublet at δ 2.37 (J = 10.5 Hz) were further split into unresolved multiplets by couplings to the C_1 and C_4 bridgehead hydrogens and by long-range couplings. The higher field half at δ 1.60 was partially obscured by other signals. Double irradiation at δ 1.60 collapsed the doublet at δ 2.37 to a singlet, confirming that this signal originates from the *syn*-C_7 hydrogen. The remaining complex signal in the region of δ 2.00-1.27 is attributable to the *anti*-C_7 hydrogen and the hydrogens at C_5 and C_6.

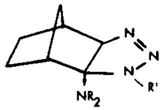
The facile decomposition of Vb and Vc in methanol, under mild conditions, to give VI and VII, respectively, prompted us to investigate the decomposition of these triazolines in more detail. Triazoline Vc was heated in aqueous methanol under reflux for 18 hours to yield a mixture consisting of about 76% of VI and 24% of VII. Estimates of the relative proportions of the epimers VI and VII in this reaction mixture, and in subsequent mixtures, were made by analysis of the 100-MHz NMR spectra of the mixtures; of particular value was the comparison of the integral of the 3-*exo* hydrogen resonance with that of the 3-*endo* hydrogen resonance, both of which are well-resolved signals. When the above reaction was terminated after 1 hour, no Vc was detected in the reaction mixture, and the product consisted of a mixture of 98.5% VII and 1.5% VI.

Treatment of triazoline Va with aqueous methanol under reflux for 1 hour produced only VII; no *endo*-3-benzamidonorbornanone (VI) could be detected. When the same reaction mixture was refluxed for 17 hours, the epimers VII and VI were obtained in a ratio of 98:2.

Triazoline Vb was also treated with aqueous methanol under reflux for 1 hour to produce a mixture of 29% VII and 71% VI.

In seeking an intermediate in the reaction of Vc leading to 3-benzamidonorbornanone, Vc was treated with absolute methyl alcohol under reflux for 18 hours to yield

TABLE I



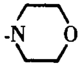
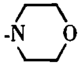
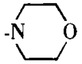
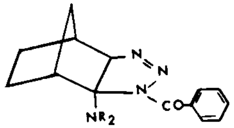
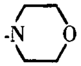
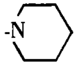
Compound	-NR_2	R′	Yield, %	M.P., °C	δ H-3a $CDCl_3$ (singlet)	Recrystallization Solvent	Formula	Analysis Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
IIIa		C_6H_5	85	136-138	3.98	Cyclohexane	$C_{17}H_{22}N_4O$	68.43	7.43	18.78	68.46	7.31	18.69
IIIb		(4) Cl-C_6H_4	84	202-204	3.91	Acetone	$C_{17}H_{21}N_4ClO$	61.32	6.36	16.84	61.27	6.40	16.72
IIIc		(4) NO_2-C_6H_4	80	203-205 dec.	4.02	Acetone	$C_{17}H_{21}N_5O_3$	59.46	6.16	20.40	59.36	6.17	20.64

TABLE II



Compound	-NR_2	Yield %	M.P., °C	δ H-3a $CDCl_3$ (singlet)	Recrystallization Solvent	Formula	Analysis Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
Va		69	136-140 dec.	3.95	Benzene-cyclohexane	$C_{18}H_{22}N_4O_2$	66.23	6.79	17.17	66.29	6.86	17.17
Vb		62	83-86	4.00	Methanol	$C_{18}H_{22}N_4O$	69.65	7.14	18.05	69.92	7.25	17.68
Vc		71	113-117 dec.	3.90	Methanol	$C_{19}H_{24}N_4O$	70.34	7.46	17.27	70.08	7.32	17.31

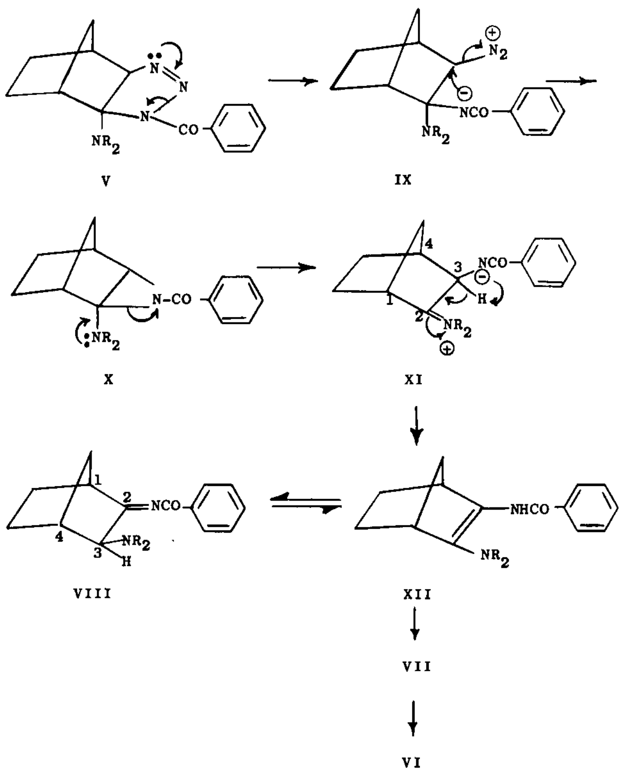
the unstable piperidinobenzoylimine VIIIc, which was extremely sensitive to moisture and which could not be obtained in a pure state. The structure of VIIIc follows from its infrared and NMR spectra. Significant in the NMR spectrum was the presence of a singlet at δ 3.65 which can be ascribed to the 3-*endo* hydrogen, indicating that this compound must be the 3-*exo* piperidino epimer. Compound VIIIc on treatment with aqueous methanol was readily converted into VII. It is noteworthy that triazoline Vc was recovered unchanged after heating in anhydrous benzene at 65-70° for 18 hours.

We also made a brief study of the thermal decomposition of Va, Vb and Vc in the absence of solvent. When triazoline Va was pyrolyzed neat at 130°, loss of nitrogen occurred, and the unstable morpholinobenzoylimine (VIIIa) resulted. Evidence for structure VIIIa was provided by its infrared and NMR spectra. Compound VIIIa was readily hydrolyzed to *exo*-3-benzamidonorbornanone (VII) in aqueous methanol. Similarly, pyrolysis of Vb and Vc at 110-120° and 120-125°, respectively, yielded the corresponding aminobenzoylimines VIIIb and VIIIc. Both VIIIb and VIIIc were readily hydrolyzed in aqueous methanol; the former afforded a mixture of VI and VII, while the latter gave only VII.

A plausible mechanism for the formation of aminobenzoylimine VIII from aminobenzoyltriazoline V involves initial formation of the diazonium-betaine intermediate IX (see Chart III) which then loses nitrogen to afford the benzoylaziridine X. Cleavage of the aziridine ring, followed by proton transfer from C_3 to nitrogen, would give the enamine XII, which could then tautomerize to afford the observed aminobenzoylimine VIII. The existence of ketimine-enamine tautomerism in similar systems has been demonstrated by Alder and Stein (18). Hydrolysis of VIII *via* the enamine XII would give *exo*-3-benzamidonorbornanone (VII) which could then be epimerized in the reaction mixture. Epimerization occurs presumably *via* enolization of the norbornanone carbonyl, the extent of epimerization being governed by the basicity of the secondary amine liberated during the hydrolysis of the enamine intermediate and by the duration of the reaction.

That *exo*-3-benzamidonorbornanone (VII) is the initially formed hydrolysis product, which is then epimerized, is supported by the following observations: (a) VII is produced as the sole product in the reaction of Va with aqueous methanol after refluxing for 1 hour, and it is the preponderant epimer in the mixture of epimers produced in the reaction of Vc with aqueous methanol under similar conditions. (b) When the above reactions are prolonged for 18 hours, *endo*-3-benzamidonorbornanone (VI) can be detected in the product derived from Va, while in the product mixture derived from Vc, VI is now the predominant epimer. Furthermore, if epimerization does occur in the reaction mixture, then it would be supposed that treatment of *exo*-3-benzamidonorbornanone (VII) with an appropriate secondary amine in refluxing aqueous methanol would result in epimerization. This was found to be the case. Treatment of *exo*-3-benzamidonorbornanone (VII) separately, with an equivalent of morpholine, piperidine and pyrrolidine in refluxing aqueous methanol for 16 hours, afforded mixtures which contained in addition to unchanged VII, 1, 72 and 85% *endo*-3-benzamidonorbornanone (VI), respectively.

CHART III



It is interesting to note that the related aminobenzoyltriazolines derived from aminocyclohexene rearrange by a different pathway which involves contraction of the cyclohexane ring (19).

EXPERIMENTAL (20)

1-Phenyl-7a-morpholino-4,7-methano-3a,4,5,6,7,7a-hexahydrobenzotriazole (IIIa).

Under a nitrogen atmosphere, a solution of phenyl azide (5.95 g., 0.05 mole) in 20 ml. of benzene was added dropwise during 15 minutes to a cold (15°) stirred solution of 2-*N*-morpholinobicyclo[2.2.1]hept-2-ene (8.95 g., 0.05 mole) in 20 ml. of benzene. The reaction was exothermic and the temperature rose to 38°. After the addition was completed, the mixture was stirred overnight at room temperature. The benzene was evaporated under reduced pressure, and the resulting white solid was washed with a little ether to afford 12.7 g. (85%) of IIIa. Recrystallization from cyclohexane furnished large colorless needles of IIIa, m.p. 136-138°. Triazolines IIIb and IIIc were prepared under the same conditions (see Table I).

1-Benzoyl-7a-pyrrolidino-4,7-methano-3a,4,5,6,7,7a-hexahydrobenzotriazole (Vb).

Under a nitrogen atmosphere, a solution of benzoyl azide (14.7 g., 0.1 mole) in 90 ml. of benzene was added dropwise during a 15-minute period to a stirred solution of 2-*N*-pyrrolidinobicyclo[2.2.1]hept-2-ene (16.3 g., 0.1 mole) in 20 ml. of benzene at 15°. The temperature rose to 25°, and after the addition was completed the mixture was stirred at room temperature for 20 hours. The benzene was removed under reduced pressure, and the resulting oil was dissolved in 80 ml. of methanol. On standing (19.1 g., 62%) of Vb, m.p. 81-84°, separated. Recrystallization from hot methanol furnished 12.1 g. of Vb, m.p. 83-86°. The mother liquor from the recrystallization was evaporated and yielded a second crop of material (3.1 g.), m.p. 120-132°, and upon further concentration a third crop of 0.9 g., m.p. 163-167°. Crops two and three were combined and recrystallized from methanol and then twice from benzene to give 1.8 g. of *endo*-3-benzamidonorbornanone (VI), m.p. 168-172°. IR (potassium bromide) 3.01 (NH), 3.25 (aromatic CH), 3.35 and 3.45 μ (CH$_2$), 5.71 (norbornanone C = O), 6.12 (secondary amide C = O), 6.25, 6.35 (aromatic C = C), 6.55 (secondary amide NH) and 14.50 μ (monosubstituted aromatic); the mass spectrum shows a molecular ion at m/e 229.11042, calcd. for $C_{14}H_{15}NO_2$, 229.11027.

Anal. Calcd. for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.72; H, 6.69; N, 6.02.

1-Benzoyl-7a-piperidino-4,7-methano-3a,4,5,6,7,7a-hexahydrobenzotriazole (Vc).

Under the same conditions used for Vb, 2-*N*-piperidinobicyclo[2.2.1]hept-2-ene (8.9 g., 0.05 mole) and benzoyl azide (7.4 g., 0.05 mole) in 80 ml. of benzene furnished 11.6 g. (71%) of Vc, m.p. 112-115° dec., (see Table II). Recrystallization from hot methanol gave 7.6 g. of Vc, m.p. 113-117° dec. Evaporation of the methanol mother liquor gave 1.6 g. of VII, m.p. 209-214°. Recrystallization from methanol and then twice from ethanol gave VII, m.p. 215-216.5°. IR (potassium bromide) 3.08 (NH), 3.28 (aromatic CH), 3.40 and 3.48 μ (CH$_2$), 5.72 (norbornanone C = O), 6.13 (secondary amide C = O), and 6.55 (secondary amide NH), 6.25, 6.35 and 6.72 (aromatic C = C), 13.80, 14.30 and 14.46 μ (monosubstituted aromatic); the mass spectrum shows a molecular ion at m/e 229.11064, calcd. for $C_{14}H_{15}NO_2$, 229.11027.

Anal. Calcd. for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.09; H, 6.66; N, 6.10.

Triazoline Va was prepared under the same conditions (see Table II).

Reaction of Triazoline Vc with Aqueous Methanol.

A solution of triazoline Vc (2.0 g., 6.17 mmoles) in 20 ml. of aqueous methanol (9:1 methanol-water) was heated under reflux for 18 hours. After about 30 minutes a solid precipitate formed and subsequently redissolved. The solvent was removed under reduced pressure, and the solid residue was recrystallized from benzene-cyclohexane mixture to give 1.0 g. of solid, m.p. 160-167°. NMR analysis (deuteriochloroform) of this material indicated that it consisted of a mixture of 24% VII and 76% VI. Evaporation of the benzene-cyclohexane mother liquor furnished a second crop of 0.17 g., m.p. 140-160°, which consisted of a mixture of 21% VII and 79% VI. The yield was 83%.

In another experiment, a solution of triazoline Vc (1.3 g., 4.01 mmoles) in 13 ml. of aqueous methanol (9:1 methanol-water) was refluxed for 1 hour. Solid which precipitated from solution after about 30 minutes was undissolved at the end of the reaction. The mixture was chilled in ice and the precipitated solid of 0.6 g., m.p. 200-214°, was collected by filtration. NMR analysis (DMF-d_6) indicated that this material was *exo*-3-benzamidonorbornanone (VII), and recrystallization from ethanol raised the melting point to 214-216°. The aqueous methanol filtrate above was evaporated to dryness *in vacuo*, and the residue was recrystallized from benzene to give 0.05 g. of a solid, m.p. 185-203°. NMR analysis (DMF-d_6) showed that this material consisted of a mixture of 15% VI and 85% VII. The yield was 71%.

Reaction of Triazoline Va with Aqueous Methanol.

A solution of triazoline Va (2.0 g., 6.14 mmoles) in 20 ml. of aqueous methanol (9:1 methanol-water) was refluxed for 17 hours. After about 30 minutes a solid precipitated from solution and remained undissolved throughout the course of the reaction. The mixture was chilled in ice and the solid of 1.1 g., m.p. 205-216°, which separated was collected by filtration. The NMR spectrum (DMF-d_6) of this material indicated that it was *exo*-3-benzamidonorbornanone (VII). One recrystallization from ethanol raised the melting point to 214-216°. The aqueous methanol filtrate above was evaporated to dryness under reduced pressure, and the resulting residue was recrystallized from benzene to afford 0.14 g. of a solid, m.p. 180-203°. The NMR spectrum (DMF-d_6) indicated that this solid was a mixture of 17% VI and 83% VII. The yield was 88%.

In another experiment, a mixture identical to that described above was heated under reflux for 1 hour to give 1.17 g. (83%) of *exo*-3-benzamidonorbornanone (VII), m.p. 208-216°. Recrystallization from ethanol furnished 1.0 g. of VII, m.p. 214-216°.

Reaction of Triazoline Vb with Aqueous Methanol.

A solution of triazoline Vb (1.0 g., 3.23 mmoles) in 10 ml. of aqueous methanol (9:1 methanol-water) was heated under reflux for 1 hour. The solution was evaporated to dryness *in vacuo*, and the residue thus obtained was recrystallized from benzene-cyclohexane mixture to give 0.43 g. of a solid, m.p. 145-170°. The NMR spectrum (DMF-d_6) revealed that this material consisted of a mixture of 29% VII and 71% VI. Evaporation of the mother liquor afforded a second crop of 0.05 g., m.p. 132-158°, which consisted of a mixture of 27% VII and 73% VI. The yield was 65%.

Reaction of Triazoline Vc with Absolute Methanol.

A solution of triazoline Vc (2.0 g., 6.17 mmoles) in 20 ml. of absolute methanol was heated under reflux for 18 hours, precautions being taken to exclude moisture. Evaporation of the methanol under reduced pressure furnished 1.4 g. (77%) of VIIIc as a pale yellow oil. IR (neat) 3.26 (aromatic CH), 3.40 and 3.50 (CH$_2$), 3.55 (NCH$_2$), 6.02 (C = N), 6.10 (amide C = O), 6.25, 6.34, 6.70 and 6.90 (aromatic C = C), 13.45 and 14.40 μ (monosubstituted aromatic); the spectrum also exhibited weak bands at 3.05 (N-H) and 5.70 μ (norbornanone C = O). NMR (deuteriochloroform), δ 8.17-7.69 and δ 7.57-7.05 (complex m, 5, aromatic hydrogens), 3.65 (s, 1, 3-*endo* hydrogen), 3.00-$\sim$2.4 (broad peak, 5, methylene hydrogens α,α' to nitrogen in the piperidino ring and C_1 bridgehead hydrogen), 2.4-2.24 (broad peak, 1, C_4 bridgehead) and 2.10-1.00 (m, 12, -(CH$_2$)$_3$- of piperidino ring and C_5, C_6 and C_7 hydrogens); the spectrum also showed a weak signal at δ 3.40 due to methanol and a weak peak at 3.50 of unknown origin.

Reaction of *exo*-3-Benzamidonorbornanone (VII) with Pyrrolidine.

A suspension of *exo*-3-benzamidonorbornanone (1.02 g., 4.41 mmoles) in 20 ml. of aqueous methanol (9:1 methanol-water) containing pyrrolidine (0.31 g., 4.37 mmoles) was heated under reflux for 16 hours. After removing the solvent under reduced pressure the residue was recrystallized from benzene to give 0.93 g. of a solid, m.p. 168-170°. The NMR spectrum (deuteriochloroform) indicated that this material was a mixture consisting of 15% VII and 85% VI.

Under similar conditions *exo*-3-benzamidonorbornanone (VII) was treated with an equivalent of morpholine and piperidine to afford product mixtures which contained in addition to unchanged VII, 1% and 72% VI, respectively.

Pyrolysis of Triazoline Vc.

Pyrolysis of Vc (3.0 g., 9.26 mmoles) at 120-125° for 4 hours afforded 2.7 g. of crude VIIIc. The NMR spectrum (deuteriochloroform at 60-MHz) of this material exhibited, in addition to the signals described for VIIIc derived from Vc in absolute methanol, unassigned peaks at δ 3.60 and 4.90; furthermore, the 3-*endo* hydrogen signal appears as a doublet (J = 1Hz). Compound VIIIc was hydrolyzed with 10 ml. of a 1:1 methanol-water mixture; refluxing for several minutes afforded after filtration and recrystallization from methanol 1.0 g. (47%) of *exo*-3-benzamidonorbornanone (VII), m.p. 214-216°.

Pyrolysis of Triazoline Va.

The title compound (3.0 g., 9.20 mmoles) was pyrolyzed at an oil bath temperature of 130° for 3 hours. The reaction product VIIIa (2.7 g.) was an orange-yellow glass. IR (potassium bromide) 3.25, 3.40, 3.53, 6.10, 6.23, 6.32, 6.68, 8.93, and 14.35 μ; NMR (deuteriochloroform) δ 8.18-7.80 and 7.64-7.24 (m, 5, aromatic hydrogens), 3.90-3.36 (m, 5, methylene hydrogens α,α' to oxygen in the morpholino ring and 3-*endo* hydrogen), 2.94-2.54 (m, 5, methylene hydrogens α,α' to nitrogen in the morpholino ring and C_1 bridgehead hydrogen), 2.52-2.34 (broad peak, 1, C_4 bridgehead) and 2.00-1.00 (m, 6, C_5, C_6 and C_7 hydrogens); the spectrum also showed an unassigned peak at δ 4.85.

Hydrolysis of VIIIa as described for VIIIc afforded after recrystallization from methanol 1.3 g. (62%) of VII, m.p. 214-216°. This material was identical with VII described above.

Pyrolysis of Triazoline Vb.

Pyrolysis of Vb (3.0 g., 9.69 mmoles) at 110-120° for 6 hours furnished 2.7 g. of crude VIIIb. IR (neat) 3.25, 3.35, 3.46, 3.50, 6.03, 6.14, 6.23, 6.40, 13.65 and 14.50 μ; NMR (deuteriochloroform) δ 8.20-7.66 and 7.60-7.00 (m, 5, aromatic hydrogens), 3.68 [d (J = 1Hz), 1, 3-*endo* hydrogen], 3.20-2.20 (m, 6, methylene hydrogens α,α' to nitrogen in the pyrrolidino ring and C_4 and C_1 bridgehead hydrogens) and 2.00-1.00 (m, 10, methylene hydrogens β,β' to nitrogen in the pyrrolidino ring and C_5, C_6 and C_7 hydrogens); the spectrum also exhibited unassigned signals at δ 3.40 and 4.80. Hydrolysis of VIIIb as described for VIIIc gave after recrystallization from methanol 0.4 g. of *exo*-3-benzamidonorbornanone (VII), m.p. 210-213°. Evaporation of the methanol mother liquor furnished a second crop of 0.65 g., m.p. 159-164°. NMR analysis (deuteriochloroform) indicated that this material was a mixture which contained about 78% *endo*- and 22% *exo*-3-benzamidonorbornanone. The combined yield (1.05 g.) was 47%.

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