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Synthesis of and Base-Induced Rearrangements in the 1,4-Diazabicyclo[4.1.0]hept-4-ene System

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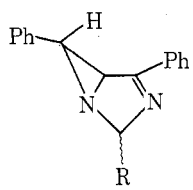
The synthesis and base-induced reactions of 2,3,5,7-tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-enes are described. These compounds are prepared from the reaction of *meso*- and *rac*-stilbenediamine with 1,3-diphenyl-2,3-dibromo-1-propanone. The assignment of stereochemistry about the ring system was made on the basis of the NMR spectra of the various structural isomers. The 1,4-diazabicyclo[4.1.0]hept-4-ene ring system was found to undergo an interesting set of reactions on treatment with base. The particular product formed was found to depend on both the initial stereochemistry of the ring system as well as on the experimental conditions used. The exo,exo isomer **4** gave 1-benzyl-2,3,5-triphenyldihydropyrazine (**10**) on treatment with potassium *tert*-butoxide. The other possible isomeric diazabicycloheptenes gave triphenylpyrazine when benzene was used as a solvent. When the reaction was carried out in *tert*-butyl alcohol, 2-benzyl-3,5,6-triphenylpyrazine (**7**), 2,3,5,7-tetraphenyl-1,4-diazacycloheptatriene (**13**), and 2,4,5,7-tetraphenyl-3,6-diazabicyclo[3.2.0]hepta-3,6-diene were isolated as the major products. The mechanistic pathways involved in the base-induced reactions are discussed.

The synthesis and cycloaddition reactions of the 1,3-diazabicyclo[3.1.0]hex-3-ene (**1**) and 1,5-diazabicyclo[5.1.0]octa-3,5-diene (**2**) systems have previously been described.[2-4] The photo- and thermal reactions encountered with these fused aziridines were readily accounted for by carbon–carbon fission of the aziridine rings of **1** and **2** to form 1,3-dipolar intermediates (azomethine ylides).[2-4] The azomethine ylides were found to undergo 1,3-dipolar cycloaddition reactions with homo and hetero multiple bonds to give a variety of heterocyclic rings.[5-9] The formation of the azomethine ylides was envisioned as an electrocyclic process proceeding by either conrotatory or disrotatory ring opening.[10] In addition, both Heine's and our own research group have described some interesting rearrangements which occur when these systems were treated with base.[2,3] As part of our continuing interest in fused aziridines, we have extended our investigations to include the 1,4-diazabicyclo[4.1.0]hept-4-ene system (**3**). The present



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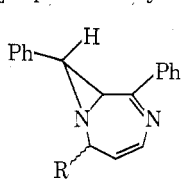

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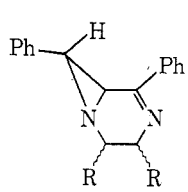

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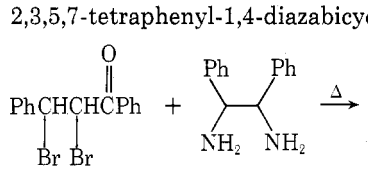
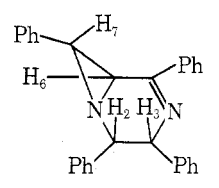
paper describes the synthesis of several 2,3-disubstituted 1,4-diazabicyclo[4.1.0]hept-4-enes and the unusual rearrangements that these systems undergo when treated with base.

Of the several possible methods to gain synthetic entry into the 1,4-diazabicyclo[4.1.0]hept-4-ene system,[11] the route involving the reaction of a dibromo ketone and a 1,2-diamine seemed most feasible. Heine and Henzel had previously demonstrated that 1-phenyl-2,3-dibromo-3-aryl-1-propanones underwent reaction with ethylenediamine and *o*-phenylenediamine to give the 1,4-diazabicyclo[4.1.0]hept-4-ene and 1,1a-dihydro-1,2-diarylazirino[1,2-*a*]quinoxaline rings.[12] When 1,3-diphenyl-2,3-dibromo-1-propanone was allowed to react with *meso*-stilbenediamine in an ethanolic solution containing triethylamine and small quantities of ammonium bromide, a mixture of four compounds was obtained. Fractional crystallization of the mixture resulted in the isolation of a crystalline solid, mp 160–161°, whose structure was assigned as (2α,3α,6α,7α)-2,3,5,7-tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-ene (**4**) on





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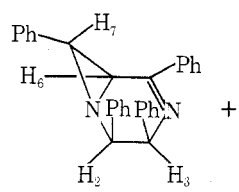

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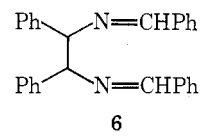

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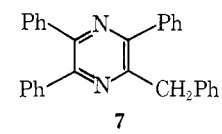

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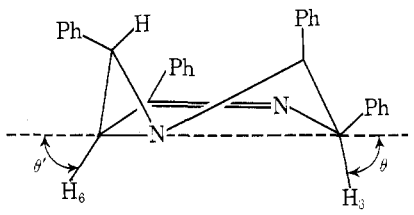
the basis of its spectral and analytical properties. The diazabicyclic **4** displayed a maximum at 252 nm (ϵ 17,000) in

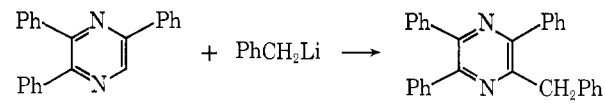
the ultraviolet region. Its NMR spectrum showed the two aziridinyl protons at τ 6.78 (H_6, d, J = 3.0 Hz) and 6.45 (H_7, d, J = 3.0 Hz), the two benzylic protons at 5.68 (H_2, d, J = 6.5 Hz) and 4.91 (H_3, d, J = 6.5 Hz), and the aromatic protons as a multiplet centered at τ 2.07–3.20. The spatial relationship of the phenyl groups was established experimentally by application of nuclear Overhauser effects.[13] Double irradiation of the signal at τ 5.68 or 4.91 gave evidence of a 17–25% intensity enhancement in the τ 6.45 peak. Accordingly, the tertiary benzylic hydrogens (H_2 and H_3) and the aziridinyl hydrogen (H_7) must be proximal, an observation which requires the spatial relationship embodied in the exo,exo isomer (**4**).

A small quantity of the isomeric (2α,3α,6β,7β)-2,3,5,7-tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-ene (**5**), mp 146–147°, was also isolated from the reaction mixture. The yield of this material could be substantially improved if the reaction conditions were slightly altered. This was done by using chloroform as the solvent and carrying out the reaction at room temperature. Under these conditions a 40% yield of diazabicyclic **5** was obtained. The NMR spectrum of **5** consisted of a doublet of doublets at τ 6.84 (H_6, J = 3.0 and 1.5 Hz), a set of doublets at τ 6.45 (H_7, J = 3.0 Hz) and 4.98 (H_2, J = 5.5 Hz), and a doublet of doublets at τ 4.50 (H_3, J = 5.5 and 1.5 Hz) as well as a 20-proton multiplet at τ 2.50–3.10. Inspection of molecular models shows that protons H_3 and H_6 for this isomer are oriented in such a manner that homoallylic coupling across the C–N double bond should be at a maximum. Examples of homoallylic coupling across a C–C double bond have been observed previously and give rise to a coupling constant which ranges from 0.2 to 1.8 Hz.[14] The magnitude of homoallylic coupling is known to be dependent on the angles θ and θ' between the plane of the C=N double bond and the C_1–H_1 and C_4–H_4 bonds, respectively.[14] The coupling magnitude will be greatest when θ and θ' are 90° and will be at a minimum when the angles are at 0°. For diazabicycloheptene **5**, protons H_3 and H_6 are oriented in such a fashion that both θ and θ' are approximately 80° in the conformation shown below. The isomeric diazabicycloheptene **4** does not exist in



a conformation where both θ and θ' have the proper angle to allow for significant homoallylic coupling. On this basis, we can distinguish between the two isomeric diazabicycloheptenes. Spin decoupling of structure **5** was also carried out in order to verify the existence of the homoallylic coupling. When the doublet of doublets at τ 4.50 (H_3) was saturated with an external field, the doublet of doublets at τ 6.84 (H_6, J = 3.0 and 1.5 Hz) collapsed to a simple doublet (J = 3.0 Hz). Similarly, double irradiation of the signal at τ 6.84 resulted in the collapse of the double doublet at τ 4.50 to a simple doublet (J = 5.5 Hz). Accordingly, the tertiary benzylic hydrogen (H_3) and the aziridinyl hydrogen (H_6) must be homoallylically coupled, an observation which requires an endo orientation of the C_3 phenyl ring.

In addition to the two isomeric 1,4-diazabicyclo[4.1.0]heptenes (**4** and **5**), two additional compounds, **6** (19%) and **7** (5%), were also isolated from the reaction of *meso*-stilbenediamine with 1,4-diphenyl-2,3-dibromo-1-propanone. Structure **6** was identified as 1,3,4,6-tetraphenyl-2,5-diazahexa-1,5-diene, mp 166–167°, by comparison with an authentic sample prepared from the reaction of *meso*-stilbenediamine with benzaldehyde. Structure **7** was assigned as 2-benzyl-3,5,6-triphenylpyrazine, mp 141–142°, on the basis of its spectral properties: uv (95% ethanol) 326 nm (ϵ 15,800), 303 (ϵ 15,200), and 272 (ϵ 15,400); NMR ($CDCl_3$) τ 5.60 (s, 2 H) and 2.20–2.76 (m, 20 H); *m/e* 398 (M^+). This structure was unambiguously verified by comparison with an authentic sample of **7** which was prepared by treating triphenylpyrazine with benzyllithium according to the general procedure of Klein and Spoerri.[15]



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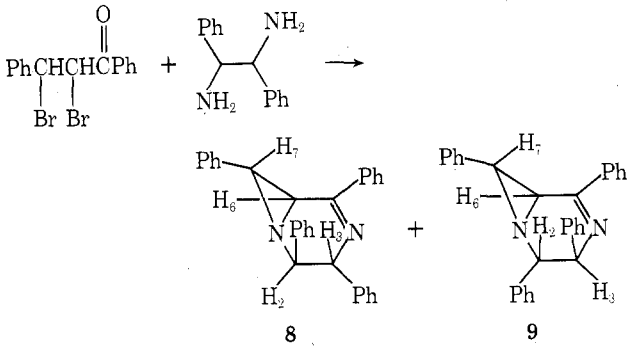
A mechanistic rationale which accounts for the formation of **6** is based on the premise that benzaldehyde is produced in small quantities during the reaction.[16] Stilbenediamine will then condense with the generated benzaldehyde to produce compound **6**. The formation of diazabicycloheptenes **4** and **5** can be conveniently rationalized by a series of reactions which are analogous to those proposed to account for the formation of *N*-alkylaroylaziridines from the reaction of dibromochalcone with alkylamines.[17] A mechanism for the formation of 2-benzyl-3,5,6-triphenylpyrazine (**7**) will be put forth at a later point in this paper.

Treatment of 1,3-diphenyl-2,3-dibromo-1-propanone with *rac*-stilbenediamine proceeded in an analogous fashion and afforded a mixture of (2α,3β,6β,7β)- and (2α,3β,6α,7α)-2,3,5,7-tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-ene (**8** and **9**). The mixture could be separated

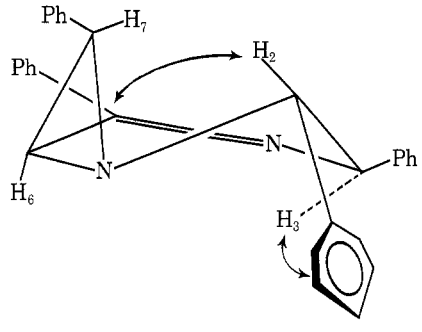


8 **9**

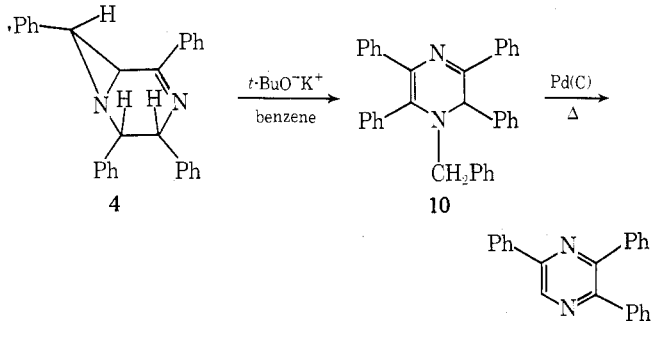
by silica gel chromatography using a 15% ether–85% cyclohexane mixture. The structure assigned to the first material obtained from the chromatography column was (2α,3β,6β,7β)-2,3,5,7-tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-ene (**8**), mp 159–160°. The NMR spectrum of **8** shows proton H_2 as a doublet at τ 6.80 (J = 9.0 Hz). This unusually high field position can be attributed to anisotropic shielding of this proton by the neighboring phenyl ring. Proton H_3 also appears as a doublet (τ 5.42, J = 9.0 Hz) and is also located at a higher field position than the corresponding proton in structures **4** or **5**. This again can be attributed to the anisotropic shielding by the neighboring phenyl group. The two aziridinyl protons appear to be magnetically equivalent, since they both appear as a singlet at τ 7.10. This equivalence can be explained by the large upfield shift experienced by proton H_7 and is undoubtedly due to the anisotropic shielding by the C_2 phenyl ring. Proton H_6 is also shielded, but to a lesser extent by the C_3 phenyl ring.

The second fraction isolated from the chromatographic separation was assigned the structure of (2α,3β,6α,7α)-2,3,5,7-tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-ene (**9**), mp 206°. The stereochemistry of this diazabicyclic system

follows from an analysis of its diagnostic NMR spectrum. The signal corresponding to proton H_2 in **9** appeared as a doublet at τ 6.40 (J = 10.0 Hz). The appearance of this proton (H_2) at a higher field relative to proton H_2 in **5** (τ 4.98) is consistent with the anisotropic shielding of this proton by the adjacent aziridine ring.[18] Proton H_3 also appears at high field as a broad doublet at τ 5.40 (J = 10.0 Hz). The high field position of H_3 can also be attributed to the shielding effect of the C_2 phenyl ring. Proton H_7 of structure **9** appears as a doublet at τ 6.04 (J = 2.0 Hz), and proton H_6 appears as a broad doublet at τ 6.60 (J = 2.0 Hz). The broad nature of the doublets assigned to protons H_3 and H_6 can be attributed to a long-range homoallylic coupling across the C–N double bond. Double irradiation of the signal at τ 5.40 resulted in the collapse of the τ 6.60 broad doublet to a clean doublet (J = 2.0 Hz). When the doublet at τ 6.04 was irradiated with an external field, the broad doublet at τ 6.60 collapsed to a broad singlet. These observations require that the stereochemistry of the phenyl ring at C_3 be located in the endo position. The most likely conformation of diazabicycloheptene **9** which accounts for the NMR data is that shown below.

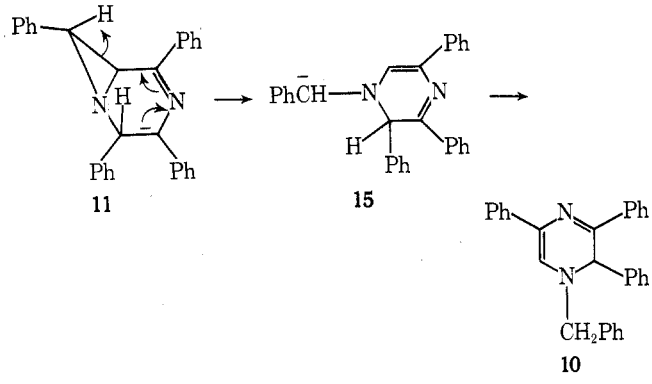


The 1,4-diazabicyclo[4.1.0]hept-4-ene ring system was found to undergo an interesting set of reactions on treatment with base. The particular product formed was found to depend on both the initial stereochemistry of the ring system as well as the experimental conditions used. Thus, treatment of diazabicycloheptene **4** with potassium *tert*-butoxide in benzene afforded a yellow solid, mp 128–129°, in good yield. This compound was assigned the structure of 1-benzyl-2,3,5-triphenyldihydropyrazine (**10**) on the basis

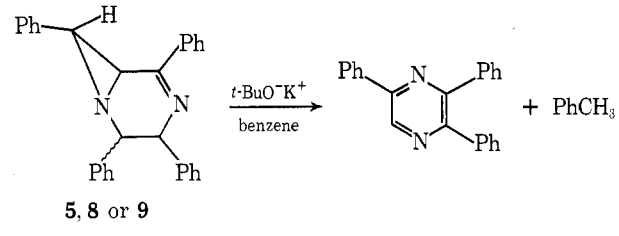


of its spectroscopic and chemical properties. The infrared spectrum of **10** showed an absorption band at 6.23 μ, characteristic of a C=N double bond. The NMR spectrum consisted of singlets at τ 4.54 (1 H) and 3.44 (1 H), an AB quartet centered at τ 5.55 (2 H, J = 14.0 Hz), and a multiplet located at τ 2.4–3.0 (20 H). The mass spectrum showed the molecular ion at m/e 400 and also exhibited a major peak at m/e 309 corresponding to the loss of a benzyl group. Chemical confirmation of this structure was obtained by dehydrogenation of **10** with palladium on charcoal to triphenylpyrazine.

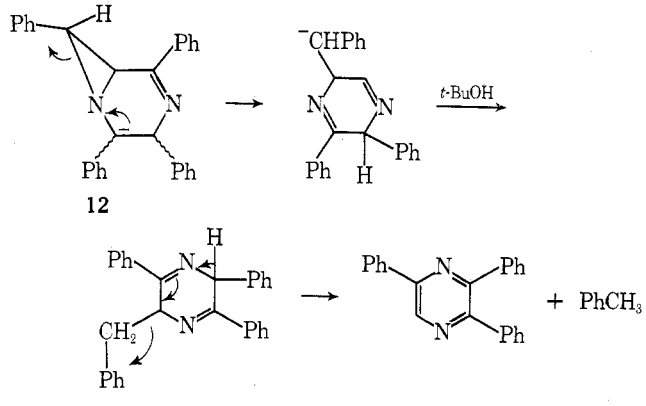
A mechanistic rationalization of the formation of **10** from the base treatment of **4** is based on the premise that the initially generated carbanion (**11**) induces carbon–carbon bond cleavage of the aziridine ring. This step is then followed by protonation to give the final product.



It is interesting to note that treatment of the isomeric 1,4-diazabicyclo[4.1.0]heptenes **5**, **8**, or **9** with potassium *tert*-butoxide, under conditions identical with those outlined above, did not produce any detectable quantities of 1-benzyl-2,3,5-triphenyldihydropyrazine (**10**). Instead, the two products formed were toluene and triphenylpyrazine.



A control experiment showed that dihydropyrazine **10** was stable under the reaction conditions. The absence of dihydropyrazine **10** from the base treatment of diazabicycloheptenes **5**, **8**, and **9** indicates that these isomers rearrange by a different pathway from that encountered with diazabicycloheptene **4**. The formation of triphenylpyrazine can be postulated to arise by carbon–nitrogen bond cleavage of the aziridine ring. The two reaction pathways differ primarily

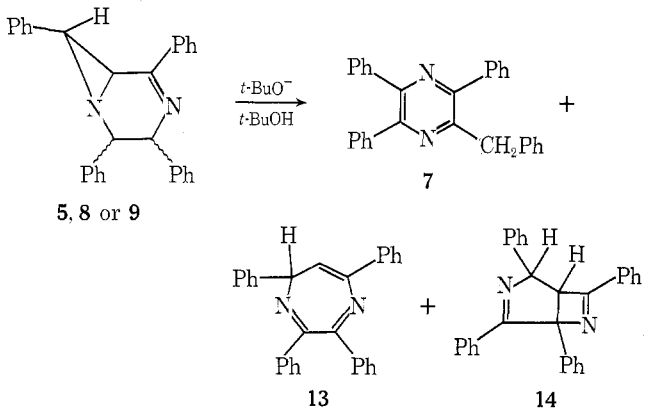


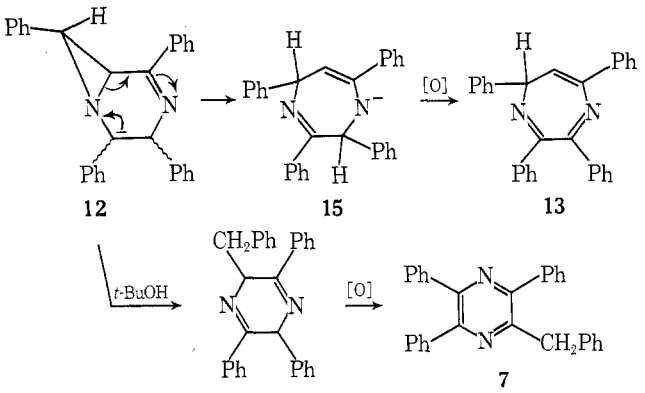
in the site of proton removal. Inspection of molecular models shows that the C_2 proton in structure **4** is situated in a sterically congested environment and consequently removal of this proton by the bulky *tert*-butoxide is sterically hindered. Instead, proton loss occurs at C_3 to generate carbanion **11**. On the other hand, proton loss with the isomeric diazabicycloheptenes (**5**, **8**, and **9**) occurs on the more accessible C_2 carbon to generate anion **12**, which subsequently undergoes carbon–nitrogen ring opening.

When the base-induced reactions of diazabicycloheptenes **5**, **8**, or **9** were carried out at 60° in the presence of *tert*-butyl alcohol, three new products were formed. The

relative yields of these three new compounds were found to vary as a function of time. Careful examination of the product distribution showed that compounds **7** and **13** were formed shortly after the addition of base. After 3 hr, the yield of **13** began to decrease while compound **14** started to appear in the reaction mixture. When the reaction was carried out at room temperature, only compounds **7** and **13** could be detected. From these observations we conclude that **7** and **13** are products which result from two separate mechanistic pathways which are operating concurrently. Further experiments showed that **13** was converted to **14** in high yield when it was heated in benzene. Compound **13** was assigned the structure of 2,3,5,7-tetraphenyl-1,4-diazacyclohepta-1,3,5-triene, mp 152–154°, on the basis of its spectroscopic properties: ir (KBr) 6.22 μ; uv (95% ethanol) 263 nm (ϵ 26,600) and 335 (4800); NMR ($CDCl_3$) τ 5.52 (s, 1 H) and 1.8–2.9 (m, 21 H); *m/e* 398 (M^+), 308, 295 (base), 103, and 77. The structure of **14** was assigned as (1α,2β,5α)-2,4,5,7-tetraphenyl-3,6-diazabicyclo-[3.2.0]hepta-3,6-diene, mp 205–206°, on the basis of a mass spectrum parent peak at *m/e* 398, infrared absorptions at 6.23 and 6.59 μ, uv absorptions at 384 (ϵ 13,900) and 257 nm (31,000), and NMR signals at τ 7.78 (1 H, d, J = 11.0 Hz) and 4.50 (1 H, d, J = 11.0 Hz) as well as a 20-proton multiplet located at τ 1.9–2.9. The chemical shift of proton H_1 (τ 7.78) in **14** is similar in position to the corresponding proton of the carbocyclic analog (2,2,6-trimethylbicyclo-[3.2.0]hepta-3,6-diene) which has been reported to have a value of τ 7.30.[19] The position of proton H_2 (τ 4.50) in structure **14** is similar to the analogous proton in 2,5-diphenyl-Δ^1-pyrroline, which has been reported to absorb at τ 4.28.[20] The observed coupling constant for the two tertiary hydrogens in **14** (J = 11.0 Hz) can be accounted for if one assumes a cis vicinal relationship between protons H_1 and H_2.[21] The formation of **14** from the thermolysis of **13** corresponds to a 4π-electrocyclic ring closure.

The ring expansion of diazabicycloheptenes (**5**, **8**, or **9**) into diazacycloheptatriene **13** is envisaged to occur by removal of the proton at C_2 to give carbanion **12**, which undergoes a subsequent ring opening in one of two directions. One direction involves a cleavage of the exocyclic C–N bond of the aziridine ring to produce a dihydropyrazine which, in this case, is preferentially oxidized to the corresponding pyrazine rather than eliminating benzyl carbanion as had been observed in the absence of *tert*-butyl alcohol. This route would also account for the formation of the small amount of **7** formed from the reaction of dibromochalcone and *meso*-stilbenediamine in 95% ethanol. The other competitive path involves cleavage of the endocyclic C–N bond of the aziridine ring to generate carbanion **15**, which is subsequently oxidized to the final product (i.e., **13**). This path is closely related to the base-induced rearrangement of 2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene to 2,4,6-triphenylpyrimidine.[2,3] Apparently, the presence of *tert*-butyl alcohol in the reaction mixture affects the reaction conditions in such a way that endocyclic C–N bond cleavage becomes competitive with exocyclic C–N ring cleavage. The reason for this is not apparent at this time and further work must be done before this point can be clarified. As expected, treatment of 1,4-diazabicycloheptene **4** with potassium *tert*-butoxide under similar reaction conditions gave no detectable quantities of structures **7**, **13**, or **14**. The only product isolated from this reaction was dihydropyrazine **10**. This result is consistent with the formation of a different carbanion (i.e., **11**) with this isomer as a consequence of the steric factors associated with proton removal.





Experimental Section

All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 100 MHz using a Jeol MH-100 spectrometer.

Reaction of Dibromodihydrochalcone with *meso*-Stilbenediamine. A mixture containing 7.28 g of dibromodihydrochalcone, 4.16 g of *meso*-stilbenediamine,[22] 6 ml of triethylamine, and 100 mg of ammonium bromide in 230 ml of 95% ethanol was heated at reflux for 2 hr. The reaction mixture was cooled to 0° and a white solid precipitated out. Recrystallization of this material from 20% benzene–80% heptane gave 1.9 g (26%) of a white solid, mp 160–161°, whose structure was assigned as (2α,3α,6α,7α)-2,3,5,7-tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-ene (**4**) on the basis of the following data.

Anal. Calcd for $C_{29}H_{24}N_2$: C, 86.96; H, 6.04; N, 7.00. Found: C, 87.04; H, 6.21; N, 7.04.

The infrared spectrum (KBr) showed absorption bands at 3.32, 6.20, 6.70, 6.90, 7.12, 7.98, 9.42, 9.70, 13.02, 13.20, 13.95, and 14.40 μ. The ultraviolet spectrum (95% ethanol) was characterized by a maximum at 252 nm (ϵ 17,000). The NMR spectrum ($CDCl_3$) showed doublets at τ 6.78 (1 H, J = 3.0 Hz), 6.45 (1 H, J = 3.0 Hz), 5.68 (1 H, J = 6.2 Hz), and 4.91 (1 H, J = 6.2 Hz) and a multiplet at τ 3.2–2.1 (20 H). The mass spectrum (70 eV) showed the molecular ion at *m/e* (rel intensity) 400 (1) and exhibited major peaks at 309 (27), 308 (85), 307 (25), 295 (84), 206 (53), 193 (63), 104 (100), and 91 (50).

The filtrate was evaporated to an oil and ether was added. Filtration of the ether slurry to remove triethylamine hydrobromide afforded an oil which was concentrated and crystallized from 95% ethanol to give 1.5 g (19%) of a white solid, mp 166–167°. The structure of this material was assigned as 1,3,4,6-tetraphenyl-2,5-diazahexa-1,5-diene (**6**) on the basis of the following data.

Anal. Calcd for $C_{28}H_{24}N_2$: C, 86.56; H, 6.23; N, 7.21. Found: C, 86.45; H, 6.35; N, 7.18.

The infrared spectrum (KBr) showed absorption bands at 3.32, 3.55, 6.18, 6.82, 6.90, 7.29, 9.20, 13.40, and 14.5 μ. The ultraviolet spectrum (95% ethanol) was characterized by a maximum at 252 nm (ϵ 34,300). The NMR spectrum ($CDCl_3$) showed a singlet at τ 5.28 (2 H) and a multiplet at τ 2.3–3.0 (20 H). The mass spectrum

(70 eV) showed the molecular ion at *m/e* (rel intensity) 388 (4) and a base peak at *m/e* 194.

An authentic sample of 1,3,4,6-tetraphenyl-2,5-diazahexa-1,5-diene (**6**) was prepared according to the procedure outlined below. A mixture containing 500 mg of *meso*-stilbenediamine and 550 mg of benzaldehyde in 25 ml of 95% ethanol was heated at reflux for 18 hr. Filtration of the solution afforded 850 mg of a white solid (82%). Recrystallization of this material from 95% ethanol gave a white solid, mp 166–167°, whose infrared spectrum was identical with that of a sample of **6** isolated from the reaction of dibromodihydrochalcone with *meso*-stilbenediamine. A mixture melting point of the two samples was undepressed at 166–167°.

Cooling the mother liquors from the reaction of dibromodihydrochalcone and *meso*-stilbenediamine deposited 2.1 g of a gummy solid which was chromatographed on a 2 × 55 cm Florisil column. The column was eluted with a 10% ethyl acetate–90% benzene mixture (200 ml) to afford 360 mg of a material which crystallized from 95% ethanol to give a white, crystalline solid, mp 141–142°. This material was assigned the structure of 2-benzyl-3,5,6-triphenylpyrazine (**7**) on the basis of the following data.

Anal. Calcd for $C_{29}H_{22}N_2$: C, 87.40; H, 5.57; N, 7.03. Found: C, 87.15; H, 5.66; N, 7.20.

The infrared spectrum (KBr) showed absorption bands at 6.69, 6.91, 7.21, 8.47, 8.75, 8.08, 9.20, 9.61, 9.71, 13.14, and 14.42 μ. The ultraviolet spectrum (95% ethanol) was characterized by maxima at 326 nm (ϵ 15,800), 303 (15,200), and 272 (15,400). The NMR spectrum ($CDCl_3$) showed a singlet at τ 5.60 (2 H) and a multiplet between τ 2.76 and 2.20 (20 H). The mass spectrum (70 eV) showed the molecular ion at *m/e* (rel intensity) 398 (100) and exhibited major peaks at *m/e* 295 (100), 191 (30), and 77 (22).

Structure **7** was further confirmed by an unequivocal synthesis. To a solution containing 0.003 mol of benzyllithium in 30 ml of dry ether was added 600 mg of triphenylpyrazine. The reaction mixture was allowed to stir at room temperature under a nitrogen atmosphere for 12 hr. The reaction mixture was then quenched with an aqueous solution of ammonium chloride and the ethereal layer was washed twice with water and dried over anhydrous magnesium sulfate. Concentration of the ether layer under reduced pressure gave a yellow oil which was subjected to preparative thick layer chromatography. The thick layer plate was developed with benzene and the band with R_f 0.44 was extracted with methylene chloride. Evaporation of the solvent left 210 mg of a white solid. Recrystallization of this material from 95% ethanol gave a white, crystalline solid, mp 141–142°. The infrared spectrum of this material was identical with that of a sample of **7** obtained from the reaction of dibromodihydrochalcone with *meso*-stilbenediamine. A mixture melting point of the two samples was undepressed at 141–142°.

The isomeric (2α,3α,6β,7β)-2,3,5,7-tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-ene (**5**) could be isolated from the reaction of dibromodihydrochalcone with *meso*-stilbenediamine when chloroform was used as the solvent. A mixture containing 7.28 g of dibromodihydrochalcone, 4.16 g of *meso*-stilbenediamine, 6 ml of triethylamine, and 100 mg of ammonium bromide in 87 ml of chloroform was allowed to stand at room temperature for 7 days. At the end of this time the solution was washed four times with water and then dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give an amber oil. The oil was taken up in 50 ml of a 17% methylene chloride–83% methanol mixture and was allowed to stand for 2 days, at which time 3.05 g of a white solid precipitated. This material was identified as (2α,3α,6α,7α)-2,3,5,7-tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-ene (**4**). The solution was filtered and the mother liquor was concentrated to give a yellow oil. Addition of 50 ml of methanol to this oil resulted in the precipitation of 2.3 g (33%) of a white solid which contained a 3:2 mixture of **4** and **5**. An 800-mg sample of the white solid was subjected to scanning liquid–liquid partition chromatography.[23] The optical density trace consisted of two major peaks. The first major component of the mixture contained 400 mg (51%) of a white solid which was recrystallized from 95% ethanol to give white needles, mp 146–147°. This material was assigned the structure of (2α,3α,6β,7β)-2,3,5,7-tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-ene (**5**) on the basis of the following data.

Anal. Calcd for $C_{29}H_{24}N_2$: C, 86.96; H, 6.04; N, 7.00. Found: C, 86.91; H, 6.29; N, 6.94.

The infrared spectrum (KBr) shows absorption bands at 3.37, 6.17, 6.67, 6.89, 7.90, 9.38, 9.65, 12.20, 12.81, 12.95, 13.37, 13.70, and 14.40 μ. The ultraviolet spectrum (in 95% ethanol) was characterized by a maximum at 248 nm (ϵ 22,500). The NMR spectrum ($CDCl_3$) was characterized by a doublet of doublets at τ 6.84 (1 H, J = 1.5, 1.0 Hz), doublets at τ 6.45 (1 H, J = 3.0 Hz) and 4.98 (1 H, J = 5.5 Hz), a broad doublet at τ 4.50 (1 H, J = 5.5 Hz), and a multiplet between τ 3.1 and 2.0 (20 H).

Reaction of Dibromodihydrochalcone with *rac*-Stilbenediamine. A mixture containing 3.6 g of dibromodihydrochalcone, 2 g of *rac*-stilbenediamine,[24] 3 ml of triethylamine, 30 mg of ammonium bromide, and 100 ml of chloroform was allowed to stand at room temperature for 7 days. At the end of this time the solution was washed four times with water and then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give 2.4 g (65%) of a yellow oil. A 1.0-g sample of the oil was chromatographed on a 2 × 45 cm Brinkman silica gel 60 column. The column was eluted with a 15% ether–85% cyclohexane mixture at a flow rate of 3 ml/min. The first fraction collected was concentrated under reduced pressure to give 440 mg of a white solid. Recrystallization from 95% ethanol gave colorless prisms, mp 159–160°, whose structure was assigned as (2α,3β,6β,7β)-2,3,5,7-tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-ene (**8**) on the basis of the following data.

Anal. Calcd for $C_{29}H_{24}N_2$: C, 86.96; H, 6.04; N, 1.00. Found: C, 86.91; H, 6.22; N, 6.94.

The infrared spectrum (KBr) showed absorption bands at 6.14, 6.70, 6.91, 7.11, 7.50, 7.69, 8.00, 8.30, 8.46, 9.11, 9.29, 9.38, 9.65, 9.85, 10.58, 10.80, 11.50, 13.10, 13.40, and 14.40 μ. The ultraviolet spectrum (95% ethanol) was characterized by a maximum of 250 nm (ϵ 19,000). The NMR spectrum ($CDCl_3$) contained a broad singlet at τ 7.10 (2 H), doublets at τ 6.80 (1 H, J = 9 Hz) and 5.42 (1 H, J = 9 Hz), and a multiplet between τ 3.1 and 2.0 (20 H).

The second fraction obtained from the column consisted of 410 mg of a white solid. Recrystallization from 95% ethanol gave colorless needles, mp 206–207°. This material was assigned as (2α,3β,6α,7α)-2,3,5,7-tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-ene (**9**) on the basis of the following data.

Anal. Calcd for $C_{29}H_{24}N_2$: C, 86.96; H, 6.04; N, 1.00. Found: C, 86.74; H, 6.17; N, 6.93.

The infrared spectrum (KBr) showed absorption bands at 6.17, 6.69, 6.89, 7.11, 7.94, 8.47, 9.22, 9.40, 9.68, 10.58, 10.79, 10.97, 11.49, 12.01, 13.10, 13.44, and 14.40 μ. The ultraviolet spectrum (in 95% ethanol) was characterized by a maximum of 247 nm (ϵ 19,400). The NMR spectrum ($CDCl_3$) contained doublets at τ 6.60 (1 H, J = 2 Hz), 6.40 (1 H, J = 10 Hz), 6.04 (1 H, J = 2 Hz), and 5.40 (1 H, J = 10 Hz) and a multiplet between τ 2.9 and 2.1 (20 H).

Treatment of (2α,3α,6α,7α)-2,3,5,7-Tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-ene (4) with Potassium *tert*-Butoxide. A solution containing 170 mg of **4** and 540 mg of potassium *tert*-butoxide in 50 ml of benzene was allowed to stir at room temperature for 5 hr. The reaction mixture was quenched with water and the organic layer was subsequently washed with water and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give 130 mg (76%) of a yellow oil. Recrystallization from 95% ethanol afforded yellow needles, mp 128–129°. The structure of this material was assigned as 1-benzyl-2,3,5-triphenyldihydropyrazine (**10**) on the basis of the following observations. The infrared spectrum (KBr) showed bands at 6.23, 6.78, 6.88, 7.02, 7.32, 7.45, 8.23, 8.62, 9.23, 9.68, 11.88, 13.00, 13.20, 13.40, 14.26, and 14.50 μ. The ultraviolet spectrum (in 95% ethanol) was characterized by maxima at 315 nm (ϵ 14,300), 258 (17,600), and 238 (18,000). The NMR spectrum ($CDCl_3$) contained singlets at τ 4.54 (1 H) and 3.44 (1 H), an AB quartet at τ 5.55 (2 H, J = 14.0 Hz), and a multiplet between τ 3.0 and 2.4 (20 H). The mass spectrum (70 eV) showed the molecular ion at *m/e* (rel intensity) 400 (16) and exhibited major peaks at *m/e* 309 (28), 308 (90), 307 (70), 295 (16), 102 (100), and 91 (96).

Anal. Calcd for $C_{29}H_{24}N_2$: C, 86.96; H, 6.04; N, 7.00. Found: C, 87.21; H, 5.85; N, 6.92.

Oxidation of 1-Benzyl-2,3,5-triphenyldihydropyrazine with Palladium on Carbon. A mixture containing 130 mg of **10** and 50 mg of 5% palladium on carbon in 50 ml of benzene was heated at reflux for 32 hr. The catalyst was removed by filtration and the filtrate was concentrated in vacuo to leave behind a yellow oil. Recrystallization of the oil from methanol gave 87 mg (87%) of a crystalline solid, mp 154–155°. The infrared and NMR spectra of this material were identical in all respects with those of an authentic sample of triphenylpyrazine.[3] A mixture melting point was undepressed at 154–155°.

Treatment of (2α,3α,6β,7β)-2,3,5,7-Tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-ene (5) with Potassium *tert*-Butoxide. A solution containing 85 mg of **5** and 270 mg of potassium *tert*-butox-

ide in 50 ml of benzene was allowed to stir at room temperature for 4 hr. At the end of this time the reaction mixture was quenched with water and the organic layer was washed with water and then dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give a yellow oil which was recrystallized from 95% ethanol to give 48 mg of a crystalline solid, mp 154–155°. The infrared spectrum of this material was identical in all respects with that of an authentic sample of triphenylpyrazine.[3] A mixture melting point was undepressed at 153–154°.

Treatment of (2α,3α,6β,7β)-2,3,5,7-Tetraphenyl-1,4-diazabicyclo[4.1.0]hept-4-ene with Potassium *tert*-Butoxide in the Presence of *tert*-Butyl Alcohol. A solution containing 85 mg of **5**, 270 mg of potassium *tert*-butoxide, and 5 ml of *tert*-butyl alcohol in 50 ml of benzene was allowed to stir at room temperature for 1 hr. The reaction mixture was quenched with water and the organic layer was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give a yellow oil. Recrystallization of this material from 95% ethanol afforded 55 mg (65%) of a yellow solid, mp 152–154°, whose structure was assigned as 2,3,5,7-tetraphenyl-1,4-diazacycloheptatriene (**13**) on the basis of the following data. The infrared spectrum (KBr) showed absorption bands at 6.22, 6.40, 6.75, 6.91, 7.78, 9.45, 9.75, 12.90, 13.10, 13.60, and 14.40 μ. The ultraviolet spectrum (95% ethanol) was characterized by maxima at 263 nm (ε 26,600) and 335 (4800). The NMR spectrum ($CDCl_3$) contained a singlet at τ 5.52 (1 H) and a multiplet between τ 2.9 and 1.8 (21 H). The mass spectrum (70 eV) showed the molecular ion at *m/e* (rel intensity) 398 (31) and exhibited major peaks at *m/e* 308 (52), 295 (100), 103 (155), and 77 (90).

When the reaction mixture was allowed to stir for 4 hr, a second product was present as evidenced by thin layer analysis. Separation of the two products could be accomplished by preparative thick layer chromatography. The thick layer plate was developed using a 20% acetone–80% hexane solution and the lower band was extracted with methylene chloride. Evaporation of the solvent left 25 mg (25%) of a white residue which was recrystallized from 95% ethanol to give a white, crystalline solid, mp 141–142°. This material was assigned the structure of 2-benzyl-3,5,6-triphenylpyrazine (**7**). The infrared spectrum of this material was identical in all respects with that of a sample of **7** obtained from the reaction of triphenylpyrazine and benzyllithium. A mixture melting point of the two samples was undepressed at 149–150°.

Preparation of (1α,2β,5α)-2,4,5,7-Tetraphenyl-3,6-diazabicyclo[3.2.0]hepta-3,6-diene. A solution containing 600 mg of **13** in 200 ml of anhydrous benzene was heated at reflux for 4 hr. Evaporation of the solvent under reduced pressure left a yellow oil which was recrystallized from 95% ethanol to give 410 mg (68%) of a light yellow, crystalline material, mp 205.5–206.5°. This material was assigned as (1α,2β,5α)-2,4,5,7-tetraphenyl-3,6-diazabicyclo[3.2.0]hepta-3,6-diene (**14**) on the basis of the following data.

Anal. Calcd for $C_{29}H_{22}N_2$: C, 87.40; H, 5.57; N, 7.03. Found: C, 86.99; H, 5.58; N, 6.92.

The infrared spectrum (KBr) showed absorption bands at 6.59, 6.68, 6.91, 6.95, 7.62, 8.08, 8.40, 9.31, 9.69, 10.09, 10.61, 12.60, 13.01, 14.05, and 14.45 μ. The ultraviolet spectrum (95% ethanol) was characterized by maxima at 348 nm (ε 13,900) and 257 (31,000). The NMR spectrum ($CDCl_3$) showed doublets at τ 7.78 (1 H, J = 11 Hz) and 4.50 (1 H, J = 11 Hz) and a multiplet between τ 2.9 and 1.9 (20 H). The mass spectrum (70 eV) showed the molecular ion at *m/e* (rel intensity) 398 (17) and exhibited major peaks at *m/e* 295 (100), 191 (19), 103 (82), and 77 (21).

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