Thermal and Photochemical Reactions in the 1,5-Diazabicyclo[5.1.0]octa-3,5-diene System[1]

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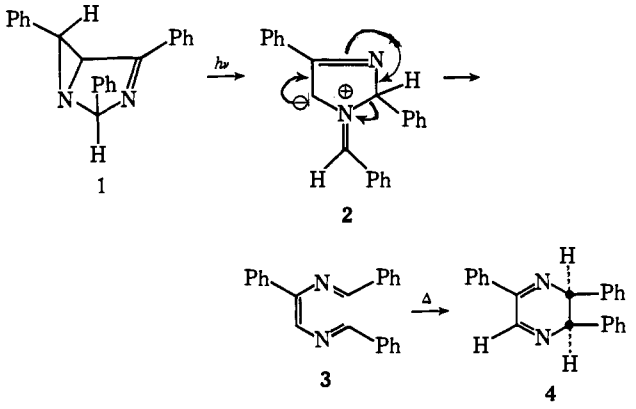
Abstract: 2,6,8-Triphenyl-1,5-diazabicyclo[5.1.0]octa-3,5-diene (**5**) was prepared by treating *trans*-2-benzoyl-3-phenylaziridine with cinnamaldehyde in an ethanolic solution saturated with ammonia. Treatment of **5** with sodium methoxide gave a high yield of *trans*-2-styryl-4,6-diphenyl-1,2-dihydropyrimidine (**6**). Ultraviolet irradiation of **5** has been found to afford four products whose structures are identified as 1,4,8-triphenyl-2,5-diazaocta-1,3,5,7-tetraene (**13**), *trans*-2-styryl-3,6-diphenyldihydropyrazine (**14**), *trans*-2-styryl-3,6-diphenylpyrazine (**15**), and 3,6-diphenyl-5,6-dihydrobenzo[*f*]quinoxaline (**16**). The formation of **16** from **5** was resolved into a sequence of four discrete reactions involving ring opening to **13**, thermal electrocyclization, photooxidation, and photocyclization. Thermolysis of **5** afforded **14**, **15**, and (6*S*)-3,7,8-triphenyl-1,4-diazabicyclo[4.1.1]octa-2,5-diene (**21**). The formation of **21** proceeds *via* an azomethine ylide formed by conrotatory opening of the aziridine ring present in **5**.

Various groups have investigated the photochemical transformations of substituted 1,3,5-hexatrienes to bicyclo[3.1.0]hex-2-enes.[3-15] Current interest in these reactions has been heightened by the awareness that orbital symmetry factors may control the various bond reorganizations to a substantial degree.[16,17] Recently, we reported on the photochemistry of the related 1,3-diazabicyclo[3.1.0]hex-3-ene system.[18] The objective of that study was to determine the role of the heteroatom in the ring opening step. The photoconversion of 2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**1**) into *cis*-2,3-dihydro-2,3,5-triphenylpyrazine (**4**) was formulated as proceeding *via* enediimine **3** which thermally cyclized to *cis*-dihydropyrazine **4**. The ring opening was shown to proceed *via* the azomethine



ylide **2**,[18,19] formed by cleavage of the aziridine C–C bond,[20] prior to the formation of **3**. An intriguing question concerned the photochemical behavior of molecules of similar structure but possessing an additional double bond as part of the ring system. One such molecule is 2,6,8-triphenyl-1,5-diazabicyclo[5.1.0]-octa-3,5-diene (**5**), which is a vinylog of the 1,3-diazabicyclo[3.1.0]hexene system. We wish to report the results of a study of the photochemistry of **5**, which was carried out in pursuit of our interest on the photochemical transformations of small ring heterocyclic systems.[21] In this paper, we also describe some of the interesting ground state reactions that were encountered with this ring system.

2,6,8-Triphenyl-1,5-diazabicyclo[5.1.0]octa-3,5-diene (**5**) was prepared by a modification of the procedure used to synthesize the 1,3-diazabicyclo[3.1.0]hexene system.[22] Starting with *trans*-2-phenyl-3-benzoylaziridine, we prepared **5** in *ca.* 25% yield by treating the trans-substituted aziridine with cinnamaldehyde in an ethanolic solution saturated with ammonia and containing small quantities of ammonium bromide. The

(1) Photochemical Transformations of Small Ring Heterocyclic Compounds. XXXVII; for part XXXVI see A. Padwa, J. Smolanoff, and S. I. Wetmore, Jr., *Chem. Commun.*, 409 (1972).
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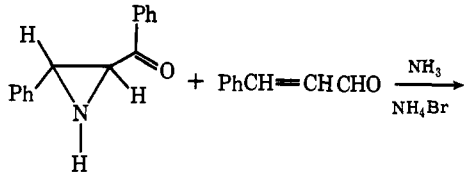
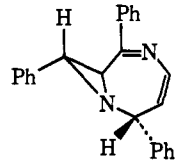
(9) (a) K. J. Crowley, *Tetrahedron Lett.*, 2863 (1965); (b) *Photochem. Photobiol.*, **7**, 775 (1968).
(10) (a) H. Prinzbach and E. Druckrey, *Tetrahedron Lett.*, 2959 (1965); (b) H. Prinzbach, H. Hagemann, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965).
(11) (a) R. C. Cookson and D. W. Jones, *J. Chem. Soc.*, 1881 (1965); (b) R. C. Cookson, S. M. De. B. Costa, and J. Hudec, *Chem. Commun.*, 1272 (1969).
(12) O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *J. Amer. Chem. Soc.*, **86**, 2660 (1964).
(13) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964).
(14) J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Amer. Chem. Soc.*, **92**, 969 (1970).
(15) H. E. Zimmerman and H. Iwamura, *ibid.*, **92**, 2015 (1970).
(16) R. B. Woodward and R. B. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(17) A. Padwa and S. Clough, *J. Amer. Chem. Soc.*, **92**, 5803 (1970).
(18) A. Padwa, S. Clough, and E. Glazer, *ibid.*, **92**, 1778 (1970); A. Padwa and E. Glazer, *Chem. Commun.*, 838 (1971).
(19) T. DoMinh and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **92**, 6997 (1970).
(20) For a review on C–C bond cleavage of the aziridine ring, see H. Heine in "Mechanisms of Molecular Migrations," Vol. III, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1971, p 145.
(21) For a review of the photochemical transformations of small ring systems see A. Padwa, *Accounts Chem. Res.*, **4**, 48 (1971).
(22) H. Heine, R. Weese, R. Cooper, and A. Durbetaki, *J. Org. Chem.*, **32**, 2708 (1967).





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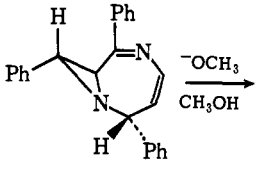
remaining 75% was a viscous gum which resisted all attempts at purification. The structure assigned to the crystalline solid obtained, mp 157–158°, was based on its method of synthesis and on several pieces of spectroscopic and chemical data. The bicyclic system **5** displays a strong maximum at 255 nm (ε 33,700) in the ultraviolet region as expected for the phenyl azadiene chromophore. Its nmr spectrum ($CDCl_3$) reveals the two aziridinyl protons at τ 7.38 and 6.40 (broad singlets), two doublets at τ 3.80 (1 H, J = 4.0 Hz) and 3.24 (1 H, J = 16.0 Hz), a doublet of doublets at τ 3.55 (1 H, J = 16.0 and 4.0 Hz), and a multiplet (15 H) in the aromatic region between τ 2.08 and 2.90. The spatial relationship of the two phenyl groups was established experimentally by application of nuclear Overhauser effects.[23] Double irradiation of the τ 3.80 doublet gave evidence of a 15–25% intensity enhancement in the τ 7.38 peak. Accordingly, the tertiary benzylic hydrogen (H_2) and the aziridinyl hydrogen (H_8) must be proximal, an observation which requires the spatial relationship embodied in the exo,exo isomer.

When a methanolic solution of **5** was treated with sodium methoxide, a near quantitative yield of *trans*-2-styryl-4,6-diphenyl-1,2-dihydropyrimidine (**6**) was obtained. The structure of **6** was established by a com-



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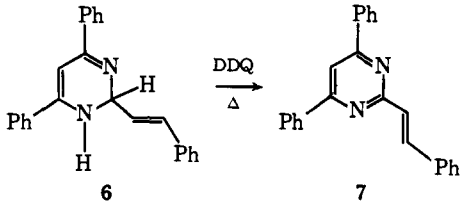

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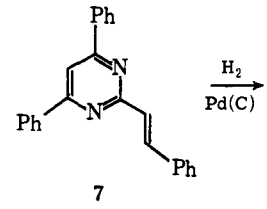
bination of spectral and chemical evidence. Structure **6** exhibits a maximum at 277 nm (ε 29,000) in the ultraviolet region and shows a broad singlet at τ 4.75, a doublet at τ 3.58 (J = 15 Hz, 1 H), and a multiplet for the remaining hydrogens between τ 2.30 and 3.02. Chemical confirmation for this structure was obtained by the oxidation of **6** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in refluxing benzene to *trans*-2-styryl-4,6-diphenylpyrimidine (**7**). Reduction of **7** over



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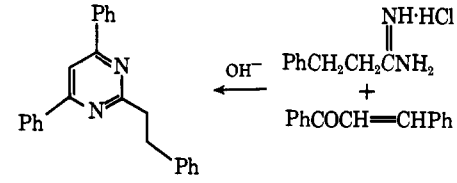

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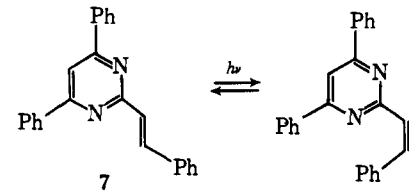
5% Pd–C gave **8**, which could be prepared independently by treating β-phenylethylamidine hydrochloride with an excess of benzalacetophenone in the presence of base according to the procedure of Dodson and Seyler.[24]

Assignment of the trans stereochemistry about the C–C double bond in **6** and/or **7** was made on the basis of thermodynamic considerations and from irradiation experiments. When **7** is irradiated in benzene and the reaction is monitored by thin layer chromatography, one sees the formation of a new isomer **9**, which could easily be isolated as a white crystalline substance, mp 122–123°. The almost identical electron spectra of **9** with that of **7** (see Experimental Section) provided supportive evidence for the indicated structure. Catalytic reduction of **9** over 5% Pd–C afforded **8**. A



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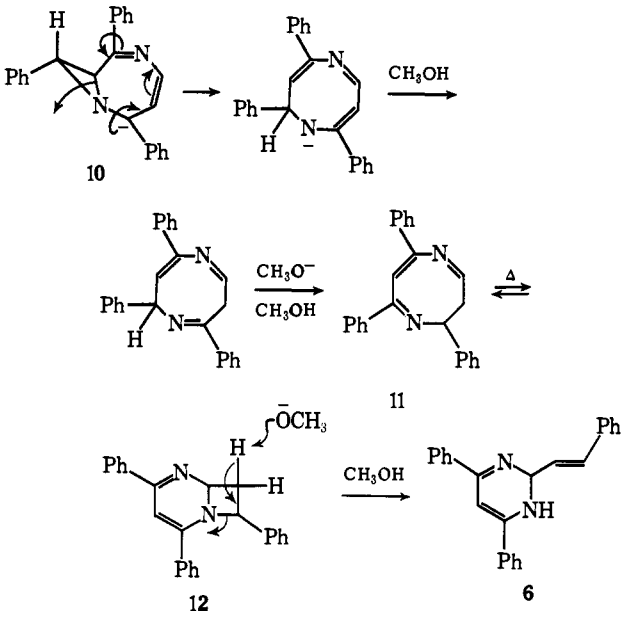
solution of **7** or **9** reached a photostationary state (**9**/**7** = 2.0/1) after 5 hr. Chemical substantiation of the cis stereochemistry of **9** was derived by iodine-catalyzed isomerization at 80°. At this temperature, **9** was converted cleanly to *trans*-styrylpyrimidine **7**.

A mechanistic rationalization of the formation of **6** from the base treatment of **5** is based on the premise that the initially generated carbanion (**10**) induces carbon–nitrogen bond breakage of the aziridine ring. This step is then followed by a series of reversible base induced 1,3-proton shifts to give **11**. Valence isomerization of **11** to its bicyclic valence tautomer **12**, followed by base-catalyzed ring opening, affords **6**. This proposal is related to the alkaline induced rearrangement of 2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-enes to triphenyl-substituted pyrimidines.[22] Although nmr studies of the reaction have failed to give evidence for the presence of valence isomers **11** or **12**, it is not unreasonable to suppose that these species are present in such small quantities that they cannot be detected spectroscopically. The passage of **12** to **6** is undoubtedly assisted by the driving force arising from relief of ring strain.

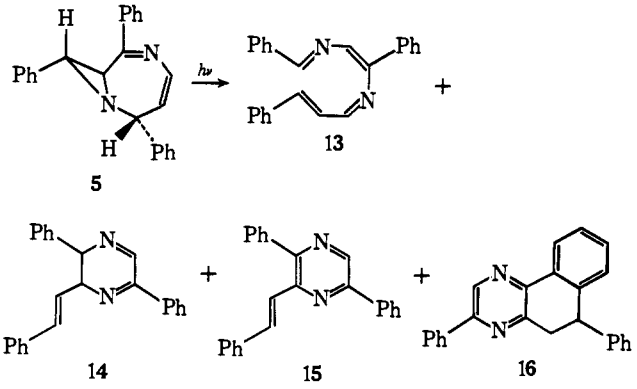
Irradiation of a solution of **5** in benzene at 50° in an immersion apparatus (Corex filter) using a 450-W

(23) For a recent review, see G. Moreau, *Bull. Soc. Chim. Fr.*, 1770 (1969).

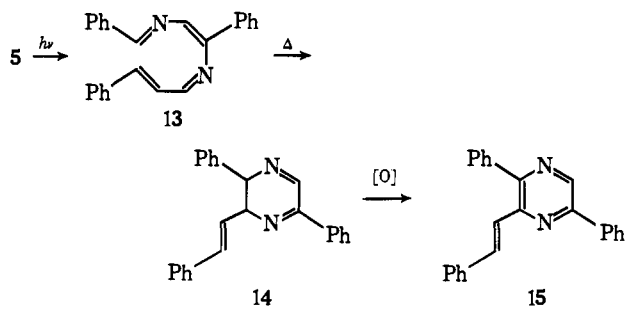
(24) R. M. Dodson and J. K. Seyler, *J. Org. Chem.*, 16, 461 (1951).

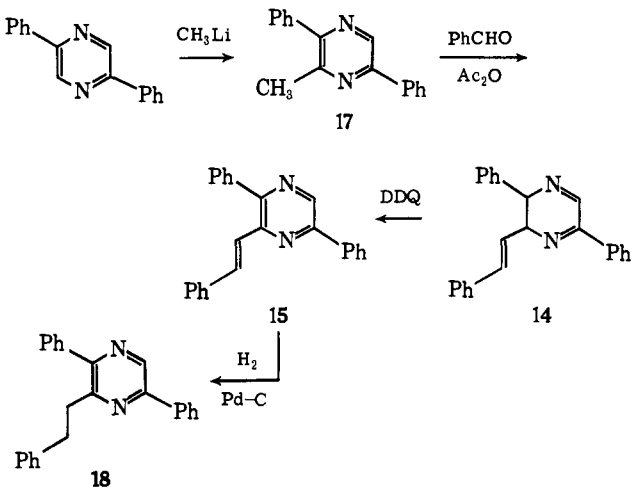


Hanovia lamp led to complete disappearance of starting material and formation of a complex mixture of photoproducts. Conventional isolational procedures afforded four products (**13**–**16**) whose relative yields varied as a function of exposure duration. Consideration of the product distribution as a function of time in a number of photolyses showed that as **13** decreased, **14** and **15** appeared, and more slowly **16** was formed.

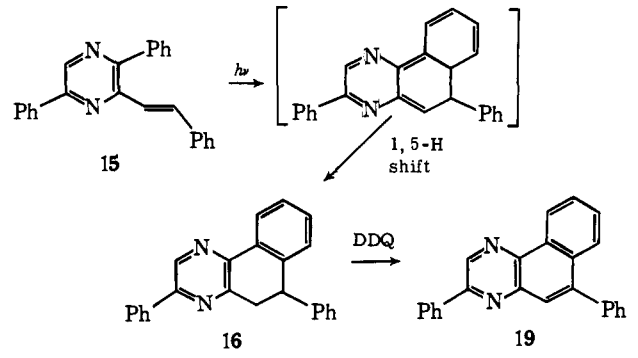


Ultraviolet irradiation of a solution of **5** in benzene for only 1.5 hr affords intermediate **13** in high yield (80%), mp 115–117°, whose structure is assigned as 1,4,8-triphenyl-2,5-diazaocta-1,3,5,7-tetraene[25] on the basis of the physical and chemical data (see Experimental Section). At 50°, thermal rearrangement of **13** took place giving **14** and **15**, but not **16**. Suspicion that compounds **14** and **15** are secondary products derived by thermal isomerization of **13** was confirmed by the finding that the photolysis of **5** in benzene at 20° gave virtually no **14**, **15**, or **16**. On warming the solution to 50° in the dark, compounds **14** and **15** were formed but not **16**. These observations require that some photochemically generated precursor of **14** and **15** persists after the light source is extinguished which then rearranges upon heating to **14** and **15**. The structures of **14** and **15** were assigned as *trans*-2-styryl-3,6-diphenyldihydropyrazine (**14**), mp 202–205°, and *trans*-2-styryl-3,6-diphenylpyrazine (**15**), mp 150–151°, on the basis of the following evidence. Oxidation of **14** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) afforded **15** in excellent yield. Structure **15** was confirmed by catalytic reduction to **18** and by its unequivocal synthesis[26] from 2,5-diphenyl-3-methylpyrazine[27] (**17**), acetic anhydride, and benzaldehyde. The trans stereochemistry about the C–C double bond in **15** was assigned on the basis of thermodynamic considerations and on the fact that **15** was recovered unchanged when heated in the presence of iodine.





Irradiation of **15** in benzene for 2 hr afforded 3,6-diphenyl-5,6-dihydrobenzo[*f*]quinoxaline (**16**), mp 148–149°, in 60% yield. The parent ion in its mass spectrum appears at *m/e* 334, indicating that **16** is isomeric with pyrazine **15**. The nmr spectrum of **16** consists of a doublet at τ 6.51 (2 H, J = 7.5 Hz), a triplet at τ 5.62 (1 H, J = 7.5 Hz), a singlet at τ 1.14 (1 H), and a 14 proton multiplet at τ 1.87–3.00 (aromatic protons). Oxidation of **16** with DDQ gave 3,6-diphenylbenzo[*f*]-quinoxaline (**19**), mp 190–191°; λ_{max} (95% ethanol)



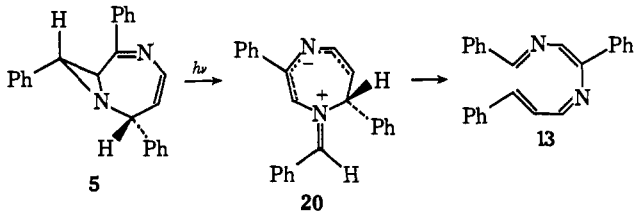
(25) The stereochemistry of 13 is unknown and is drawn in the above way only for convenience of representation.

(26) R. Roger, *J. Chem. Soc.*, 560 (1947).

(27) 2,5-Diphenyl-3-methylpyrazine was prepared by treating 2,5-diphenylpyrazine with methyllithium according to the procedure of B. Klein and P. E. Spoerri, *J. Amer. Chem. Soc.*, 72, 1844 (1950).

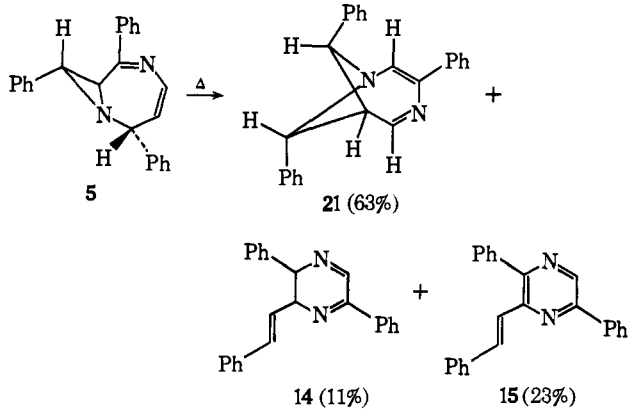
293, 253, 221 nm (ε 36,500, 30,700, 35,000) providing supportive evidence for the indicated structure.

The isolation of **16** from the extended irradiation of **5** can now be resolved into a sequence of four discrete reactions. The first step is the light induced 6 + 2 cycloreversion of **5** to 2,5-diazaoctatetraene (**13**). If concerted, this step can be viewed as either a $_{\pi}6_{s} + {}_{\pi}2_{s}$ or a $_{\pi}6_{a} + {}_{\pi}2_{a}$ process.[16] Alternatively, as was noted in the 1,3-diazabicyclic system,[18,19] the opening may proceed in a stepwise manner *via* the formation of an azomethine ylide (**20**) which subsequently opens to diazaoctatetraene **13**. The second step involves a



thermal electrocyclization of **13** to **14** which is similar in nature to the valence isomerization encountered with 1,8-diphenyl-1,3,5,7-octatetraene.[28] Under the photolytic conditions, **14** is partially oxidized to pyrazine **15**. The final step, involving the conversion of **15** to **16**, is analogous to the photochemical isomerization of 1,3,5-hexatrienes to the corresponding cyclohexa-1,3-dienes.[3] The above results indicate the difficulty of interpreting a complex photochemical reaction (*i.e.*, **5** → **16**) without at least a knowledge of the number of excitation steps involved and the sequence of these excitations.

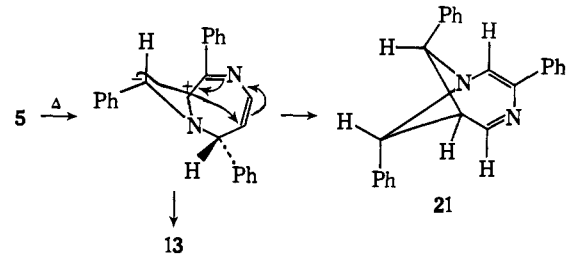
At this point, we were prompted by the somewhat unusual structure of **5** to examine its thermochemical behavior. Previous studies of substituted bicyclo[4.1.0]hepta-2,4-dienes[29] and bicyclo[6.1.0]nona-2,4,6-trienes[30,31] pyrolyses have revealed a marked propensity for skeletal rearrangement. These structural changes involve a shift of the bridge carbon atom and are of considerable interest. When **5** was heated in refluxing xylene, three compounds were produced. Approximately one-third of the mixture consisted of **14** (11%) and **15** (23%). The remaining component is considered to be (6*S*)-3,7,8-triphenyl-1,4-diazabicyclo[4.1.1]octa-2,4-diene (**21**) (65%), mp 118–119°, on the basis of



(28) E. N. Marvell and J. Seubert, *Tetrahedron Lett.*, 1333 (1969).
(29) J. A. Berson, *Accounts Chem. Res.*, 1, 152 (1968).
(30) A. G. Anastassiou and B. Y. Chao, *Chem. Commun.*, 979 (1971).
(31) F. G. Klarner, *Tetrahedron Lett.*, 3611 (1971).

the following spectral evidence. The mass spectrum (M = 336) and elemental analysis confirmed that **21** was an isomer of **5**. The ultraviolet absorption (95% ethanol) λ_{max} 285 nm (ε 21,500) was typical of a 2-phenylazadiene chromophore. The nmr spectrum showed a doublet of doublets at τ 7.24 (2 H, J = 8.0 and 1.5 Hz), a quartet at τ 4.35 (1 H, J = 8.0 Hz), and multiplets at τ 3.42 (1 H), 3.05 (1 H), and 2.75 (15 H). When the quartet at τ 4.35 was saturated with an external field, the doublet of doublets at τ 7.24 collapsed to a broad singlet. When the multiplet at τ 3.42 was irradiated with an external field, the multiplet at τ 3.05 collapsed to a triplet (J = 1.5 Hz), the quartet at τ 4.35 collapsed to a triplet (J = 8.0 Hz), and the doublet of doublets collapsed to a doublet (J = 8.0 Hz). Application of an external field at τ 7.24 resulted in the collapse of the quartet at τ 4.35 to a doublet (J = 8.0 Hz).

Reasonable mechanistic options for these thermal rearrangements involve concerted pathways or stepwise processes. The thermal rearrangement of **5** to **21** is the formal result of a suprafacial 1,5-sigmatropic shift, proceeding with retention of configuration of the migrating group, and is orbital symmetry allowed.[29] The formation of **14** (and consequently **15** by oxidation) can be attributed to thermal electrocyclization of the initially formed diazaoctatetraene **13**. If concerted, the thermal ring opening of **5** to **13** can be analyzed as a $_{\sigma}2 + {}_{\sigma}2 +$

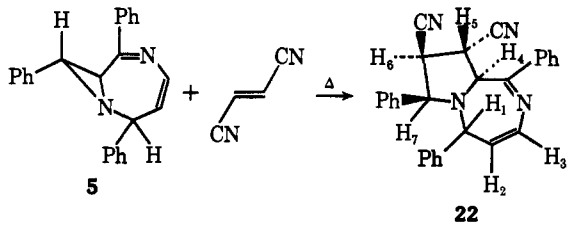


$_{\pi}2 + {}_{\pi}2$ process having an odd number of suprafacial components.[16] These thermal rearrangements may proceed, however, *via* a stepwise process involving an azomethine ylide, formed by rupture of the weak C–C bond of the aziridine ring. Since azomethine ylides are known to undergo 1,3-dipolar addition reactions,[32–36] it was anticipated that a dipolarophile might be used to capture the intermediate azomethine ylide and substantiate the stepwise mechanism of the above reactions. On the other hand, if the above reactions involve concerted bond reorganizations, no thermal adduct would be obtained when the thermolysis is carried out in the presence of a reactive dipolarophile.

The expectation that the thermal isomerization of **5** to **13** and **21** proceeded *via* an azomethine ylide was con-

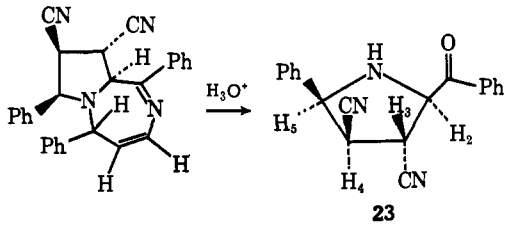
(32) H. W. Heine and R. Peavy, *ibid.*, 3123 (1965); *J. Org. Chem.*, 31, 3924 (1966); H. W. Heine, A. B. Smith, and J. D. Bower, *ibid.*, 33, 1097 (1968); H. W. Heine and R. Henzel, *ibid.*, 34, 171 (1969).
(33) A. Padwa and L. Hamilton, *Tetrahedron Lett.*, 4363 (1965); *J. Heterocycl. Chem.*, 4, 118 (1967); A. Padwa and W. Eisenhardt, *Chem. Commun.*, 380 (1968).
(34) R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, 89, 1753 (1967); R. Huisgen, W. Scheer, G. Szeimies, and H. Huber, *Tetrahedron Lett.*, 397 (1966); R. Huisgen, W. Scheer, and H. Mader, *Angew. Chem., Int. Ed. Engl.*, 8, 602 (1969); *ibid.*, 2, 633, 644 (1963); R. Sustmann, R. Huisgen, and H. Huber, *Chem. Ber.*, 100, 1802 (1967); J. H. Hall and R. Huisgen, *Chem. Commun.*, 1187 (1971); *ibid.*, 1188 (1971).
(35) J. W. Lown, G. Dallas, and T. W. Maloney, *Can. J. Chem.*, 47, 3557 (1969); *ibid.*, 4335 (1969); *Chem. Commun.*, 1543 (1968); 247 (1971).
(36) P. B. Woller and N. H. Cromwell, *J. Heterocycl. Chem.*, 5, 579 (1968); *J. Org. Chem.*, 35, 888 (1970).

firmed by its 1,3-dipolar activity in undergoing cycloaddition with an added dipolarophile. Heating **5** with fumaronitrile in boiling xylene afforded an excellent yield of the crystalline 2,6,10-triphenyl-8,9-dicyano-1,5-diazabicyclo[5.3.0]deca-3,5-diene (**22**). Most im-



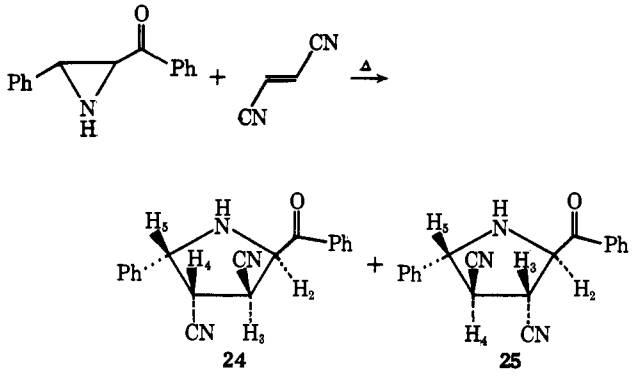
portantly, no detectable quantities of **14**, **15**, or **21** were observed in this experiment. The nmr spectrum of the adduct showed a two proton multiplet at τ 6.69 (H_5 and H_6), a multiplet at τ 5.98 (H_7), a doublet of doublets at τ 4.87 (H_4, J = 6.0 and 4.0 Hz), a multiplet at τ 4.50 (H_1), a doublet of doublets at τ 3.98 (H_2, J = 15.5 and 5.0 Hz), a doublet at τ 3.50 (H_3, J = 15.5 Hz), and a 15 proton multiplet between τ 2.06 and 2.80.

The action of aqueous hydrochloric acid converted **22** into *r*-2-benzoyl-*t*-3,*c*-4-dicyano-*c*-5-phenylpyrrolidine (**23**). A comparable amount (75%) of cinna-

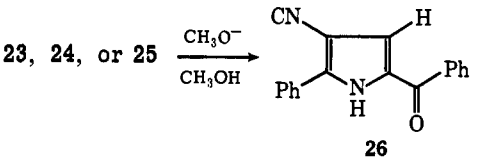


maldehyde was also formed in the hydrolysis. The stereochemical relationship of the protons on the pyrrolidine ring (**23**) is readily ascertained by an examination of the nmr spectrum which showed a triplet at τ 6.82 (H_4, J = 9.0 Hz), a doublet of doublets at τ 6.20 (H_3, J = 9.0 and 5.5 Hz), a doublet at τ 5.62 (H_5, J = 9.0 Hz), a doublet at τ 4.88 (H_2, J = 5.5 Hz), and the aromatic protons between τ 2.0 and 2.80 (10 H). The observed coupling of $J_{4,5}$ = 9.0 Hz and $J_{2,3}$ = 5.5 Hz is in good agreement with reported values for cis and trans vicinal couplings in pyrrolidines.[36] The large trans vicinal coupling constant for C_3H and C_4H (J_{34} = 9 Hz) is also in agreement with values reported in the literature.[34,36]

The assignment of the configuration of **23** (and consequently adduct **22**) was supported by comparison of its nmr spectrum with that of **24** and **25**. Pyrrolidines **24** and **25**, which were wanted for spectral comparison,

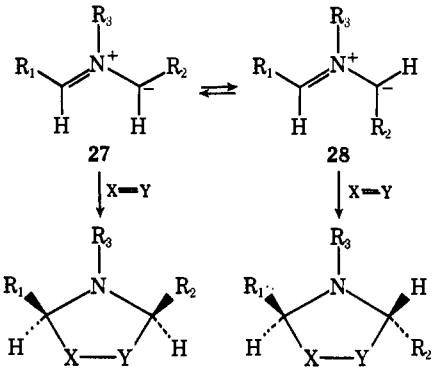


were prepared from *trans*-2-phenyl-3-benzoylaziridine and fumaronitrile. The observed coupling constant (J_{23} = J_{34} = J_{45}) of 8.0 Hz in **24** supports the assigned stereochemistry. Coupling constants (J_{23} = J_{45}) of 6.0 and J_{34} = 4.0 Hz indicate that all the hydrogens are trans in adduct **25**. Treatment of all three pyrrolidines (**23**, **24**, or **25**) with sodium methoxide in methanol afforded 2-benzoyl-4-cyano-5-phenylpyrrole (**26**),



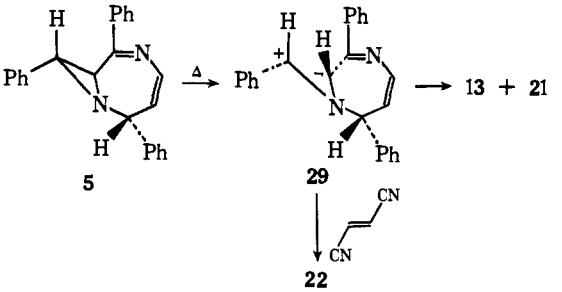
thereby supporting the gross structure of the pyrrolidine ring.

Reactions involving the thermal and photochemical cleavage of aziridines to azomethine ylides and their subsequent 1,3-dipolar additions to reactive carbon–carbon multiple bonds are well known.[32-36] Huisgen and coworkers have firmly established that the thermal ring cleavage of aziridines involves stereospecific, conrotatory ring opening. Isomerization of the less reactive *cis*-azomethine ylide **27** to the trans form **28** can



compete with cycloaddition when dipolarophiles of low activity are used.[37,38]

From the structure of the thermal adduct **22**, it seems reasonable to assign the cis structure **29** to the ylide obtained from thermolysis of **5**. Consequently, the thermal induced ring opening of **5** appears to involve a conrotatory motion which is allowed from the ground state. In the absence of a dipolarophile, ylide **29** rearranges to give products **13** and **21**. It is inter-



esting to note that *trans*-2-benzoyl-3-phenylaziridine reacted with fumaronitrile to yield cycloadducts with a trans relationship of the benzoyl and phenyl groups in the 2 and 5 positions. In the present investigation with

(37) R. Huisgen and H. Mader, *J. Amer. Chem. Soc.*, **93**, 1777 (1971).
(38) H. Hermann, R. Huisgen, and H. Mader, *ibid.*, **93**, 1779 (1971).

2-benzoyl-3-phenylaziridine, isomerization of the cis-substituted azomethine ylide **27** to the trans form **28** appears to precede the 1,3-dipolar addition. Similar results have been observed by Cromwell and Woller in the cycloaddition of methyl-1-alkyl-2-aryl-3-aziridine carboxylates with fumaronitrile.[36]

Experiments designed to trap an azomethine ylide (*i.e.*, **20**) from the irradiation of **5**, using fumaronitrile or dimethylacetylene dicarboxylate as dipolarophiles, were unsuccessful. Failure to trap an ylide on irradiation of **5** does not necessarily reject this species as a reaction intermediate. The absence of a photocycloadduct may be due to the facile unimolecular opening of **20** to **13**. Alternatively, an azomethine ylide may not be required if the photoreaction of **5** is a dissociative process which occurs instantenously upon electronic excitation.

Experimental Section[39]

2,6,8-Triphenyl-1,5-diazabicyclo[5.1.0]octa-3,5-diene (5). To a mixture of 10 g of *trans*-2-phenyl-3-benzoylaziridine[40] and 5.0 g of ammonium bromide in 200 ml of absolute ethanol was added 36 ml of cinnamaldehyde. The mixture was cooled to 20° and dry ammonia was passed through the solution for 2 hr. The mixture was allowed to stand at room temperature for 12 hr. The precipitate that formed was recrystallized from 95% ethanol to give 2.9 g (22%) of colorless prisms, mp 157–158°. The structure of this material was assigned as 2,6,8-triphenyl-1,5-diazabicyclo[5.1.0]octa-3,5-diene (**5**) on the basis of the following data.

Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.61; H, 6.11; N, 8.25.

The infrared spectrum (KBr) shows absorptions at 6.23, 6.35, 6.81, 7.25, 7.62, 8.63, 9.01, 10.30, 12.90, and 14.50 μ. The ultraviolet spectrum (in 95% ethanol) was characterized by a maximum at 255 nm (ϵ 33,700). The nmr spectrum ($CDCl_3$) was characterized by broad singlets at τ 7.38 (1 H) and τ 6.40 (1 H), a doublet at τ 3.80 (1 H, J = 4 Hz), a doublet of doublets at τ 3.55 (1 H, J = 16, 4.0 Hz), a doublet at τ 3.24 (1 H, J = 16 Hz), and a multiplet between τ 2.08 and 2.90 (15 H). The mass spectrum (70 eV) indicated a molecular ion at *m/e* (relative intensity) 336 (49), 335 (66), 334 (100), 333 (82), and exhibited major peaks at 257 (50), 245 (13), and 102 (57).

Treatment of 2,6,8-Triphenyl-1,5-diazabicyclo[5.1.0]octa-3,5-diene (5) with Sodium Methoxide. A solution of 2 g of **5** in 600 ml of freshly prepared 0.12 *N* sodium methoxide–methanol solution was allowed to stir at room temperature for 5 hr. The reaction mixture was diluted with water and extracted with ether. The ethereal layer was washed with water and dried over anhydrous magnesium sulfate, and the solvent was removed *in vacuo* to give 1.9 g of a yellow oil. Recrystallization from isopropyl alcohol afforded yellow needles, mp 130–132°, whose structure is assigned as 2-styryl-4,6-diphenyl-1,2-dihydropyrimidine (**6**) on the basis of the following observations. The infrared spectrum (KBr) had maxima at 3.15, 3.35, 6.12, 6.20, 6.70, 7.7, 7.8, and 14.5 μ. The ultraviolet spectrum showed a maximum at 277 mμ (ϵ 29,600). The nmr spectrum ($CDCl_3$) showed a doublet at τ 3.58 (1 H, J = 15.5 Hz), a broad singlet at τ 4.75 (2 H), and a multiplet between τ 2.30 and 3.02 (17 H). The mass spectrum (70 eV) showed the parent ion at *m/e* 336 and had prominent peaks at 334, 333 (base), 259, 232, 154, and 129.

Oxidation of 2-Styryl-4,6-diphenyl-1,2-dihydropyrimidine (6). A mixture of 100 mg of 2-styryl-4,6-diphenyl-1,2-dihydropyrimidine (**6**) and 80 mg of 2,3-dichloro-5,6-dicyanobenzoquinone in 50 ml of benzene was allowed to reflux for 3.5 hr. The solid that formed was removed by filtration and the mixture was concentrated to give a dark oil. Preparative thick layer chromatography[41] of the mixture produced only a single component which was recrystallized from 95% ethanol to afford a white solid, mp 129–130° (86%). The structure of this material is assigned as *trans*-2-styryl-4,6-diphenylpyrimidine (**7**) on the basis of the evidence presented below.

Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.16; H, 5.48; N, 8.30.

The infrared spectrum of this material in a potassium bromide pellet shows bands at 6.12, 6.37, 6.55, 6.93, 7.35, 9.23, 10.13, 10.25, 11.46, 11.63, 12.15, 13.13, and 14.16 μ. The ultraviolet spectrum in 95% ethanol was characterized by maxima at 308 mμ (ϵ 39,000) and 270 (36,200). The nmr spectrum ($CDCl_3$) shows a singlet at τ 2.35 (1 H) and a multiplet from τ 1.69 to 2.82 (17 H). The mass spectrum (70 eV) indicated a molecular ion at *m/e* 334 (base) and had major peaks at 231, 129, 128, 102, and 77.

trans-1-Styryl-4,6-diphenylpyrimidine was also obtained by the treatment of **5** with base. A mixture of 2 g of **5** was dissolved in 600 ml of a freshly prepared 0.12 *N* sodium methoxide–methanol solution and was allowed to stir at room temperature for 1 week. The mixture was diluted with water and extracted with ether. The ethereal layer was dried over magnesium sulfate. Removal of the solvent *in vacuo* afforded a light yellow oil which was chromatographed on a 4 × 90 cm column of silica gel, slurry packed in ethyl acetate–benzene (5–95%). The column was eluted with the above mixture and the eluent, in 50-ml fractions, was concentrated and dried *in vacuo*. The crystalline solid obtained (1.6 g, 82%), mp 129–130°, was identical in all respects with *trans*-1-styryl-4,6-diphenylpyrimidine (**7**) obtained from the oxidation of **6**.

Catalytic Hydrogenation of *trans*-2-Styryl-4,6-diphenylpyrimidine (7). In order to establish the structure of *trans*-2-styryl-4,6-diphenylpyrimidine, this material was hydrogenated to 2-(2-phenylethyl)-4,6-diphenylpyrimidine (**8**). A mixture of 1 g of **7** in 200 ml of dry methanol was hydrogenated in a Parr shaker over 0.1 g of 10% platinum on carbon at 40 psig for 10 min. The catalyst was removed by filtration and the filtrate concentrated *in vacuo* to leave a white solid which was recrystallized from 95% ethanol to give 0.87 g (86%) of 2-(2-phenylethyl)-4,6-diphenylpyrimidine (**8**), mp 124–125°.

Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.41; H, 5.92; N, 8.13.

The infrared spectrum (KBr) showed bands at 6.30, 6.56, 7.34, 8.10, 9.71, 12.16, 13.53, and 14.53 μ. The ultraviolet spectrum (in 95% ethanol) showed maxima at 288 mμ (ϵ 17,700) and 248 (23,500). The nmr spectrum ($CDCl_3$) was characterized by a broad singlet at τ 6.68 (4 H), a singlet at τ 2.37 (1 H), and a multiplet centered at τ 7.50 (15 H). The mass spectrum (70 eV) exhibited a molecular ion at *m/e* 336 and prominent peaks at 259, 232, 129, 105, 91, and 69.

Structure **8** was further confirmed by an unequivocal synthesis. A mixture of 4.0 g of β-phenylethylamidine hydrochloride and 9.05 g of benzalacetophenone in 50 ml of 95% ethyl alcohol was stirred at room temperature. To the above solution was added a solution of 2.5 g of potassium hydroxide in 50 ml of 95% ethanol. The resulting mixture was heated to reflux for 2.5 hr and the solid obtained was collected by filtration, washed with water, and recrystallized by ethanol to give 5.9 g (78%) of white needles, mp 124–125°. The infrared spectrum of this material was identical in all respects with that of a sample of **8** obtained from the reduction of **7**. A mixture melting point of the two samples was undepressed at 123–124.°

Irradiation of *trans*-2-Styryl-4,6-diphenylpyrimidine in Benzene. A solution of 500 mg of **7** in 400 ml of benzene was irradiated with an internal water-cooled mercury arc lamp (Hanovia Type L, 450 W) with a Corex filter for 4.5 hr. Concentration of the solution *in vacuo* left a mixture of two compounds which could be separated by preparative thick layer chromatography. The slower moving component (R_f = 0.36) was identified as starting material. The fast moving component (R_f = 0.56) was identified as *cis*-2-styryl-4,6-diphenylpyrimidine (**9**). Recrystallization of **9** from 95% ethanol afforded 325 mg (65%) of white needles, mp 122–123°.

Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.08; H, 5.45; N, 8.30.

The infrared spectrum (KBr) was characterized by bands at 6.34, 6.70, 7.33, 7.51, 8.10, 11.46, 12.05, 12.73, 13.82, and 14.54 μ. The ultraviolet spectrum (95% ethanol) showed a maximum at 263 mμ (ϵ 33,000). The nmr spectrum ($CDCl_3$) showed a broad singlet at τ 3.08 (2 H) and multiplets centered at τ 2.68 and 2.25 (16 H). The

(39) Melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. 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 60 MHz with the Varian Associates high-resolution spectrophotometer. Tetramethylsilane was used as an internal standard.

(40) (a) N. H. Cromwell, R. D. Babson, and C. A. Harris, *J. Amer. Chem. Soc.*, 65, 312 (1943); (b) A. E. Pohland, R. C. Badger, and N. H. Cromwell, *Tetrahedron Lett.*, 4369 (1965); (c) A. Padwa and W. Eisenhardt, *J. Org. Chem.*, 35, 2472 (1971).

(41) Thick layer plates were prepared by spreading a slurry of 150 g of Merck PF 254 + 256 silica gel and 350 ml of distilled water onto 20 × 20 cm glass plates to an average thickness of 1.5 mm. The plates were allowed to dry at room temperature for 24 hr prior to use.

mass spectrum (70 eV) indicated a molecular ion at *m/e* 334 and prominent peaks at 333 (base), 257, 231, 128, 102, and 77.

The structure of **9** was confirmed by catalytic reduction to **8** and by cis–trans photoisomerization to **7**. The photostationary state ratio of **9**:**7** was 2:1. The cis stereochemistry of **9** was established by a thermal iodine-catalyzed isomerization back to **7**. A mixture of 25 mg of **9** and 2 mg of iodine in 30 ml of benzene was heated to reflux for 48 hr. The benzene layer was washed with a 5% sodium thiosulfate solution, followed by water. The solution was then dried over sodium sulfate and the solvent was removed under reduced pressure. The infrared spectrum of the resulting solid was identical in all respects with that of a sample of **7**. A mixture melting point of the two samples was undepressed at 129–130°.

Irradiation of 2,6,8-Triphenyl-1,5-diazabicyclo[5.1.0]octa-3,5-diene (5) in Benzene. A solution of 500 mg of **5** in 400 ml of benzene was irradiated with an internal water-cooled mercury arc lamp (Hanovia Type L, 450 W) with a Corex filter for 1.5 hr. Purified nitrogen was passed through the solution for at least 45 min before irradiation commenced, and a positive pressure of nitrogen was maintained throughout. Removal of the solvent under reduced pressure gave an orange solid which was recrystallized from ethyl acetate–hexane to give 400 mg (80%) of a yellow powder, mp 115–117°. The structure of this material is assigned as 1,4,8-triphenyl-2,5-diazaocta-1,3,5,7-tetraene (**13**) on the basis of the following observations. The infrared spectrum (KBr) was characterized by a series of bands at 6.12, 6.20, 6.72, 6.91, 7.24, 7.97, 9.92, 10.03, 11.21, 12.10, 13.03, 13.24, and 14.51 μ. The ultraviolet spectrum (95% ethanol) had maxima at 295 mμ (ϵ 53,800) and 360 (26,400). The nmr spectrum ($CDCl_3$) showed a multiplet between τ 2.08 and 3.05. The mass spectrum (70 eV) showed the parent ion at *m/e* 336 and had prominent peaks at 335, 334 (base), 333, 258, 257, 245, 115, 102, and 91.

Thermolysis of 1,4,8-Triphenyl-2,5-diazaocta-1,3,5,7-tetraene (13). A solution of 200 mg of **13** in 125 ml of benzene was heated at reflux for 12 hr. Evaporation of the solvent afforded an orange oil which was fractionally crystallized to give two components. The less soluble component was recrystallized from acetone to give 110 mg (55%) of *trans*-2-styryl-3,6-diphenyl-2,3-dihydropyrazine (**14**), mp 202–205°. The infrared spectrum of this material (potassium bromide pellet) was characterized by bands at 6.27, 6.72, 6.93, 7.40, 8.13, 8.39, 9.35, 10.20, 10.39, 13.03, 13.44, 14.41, and 14.57 μ. The ultraviolet spectrum (95% ethanol) had maxima at 295 mμ (ϵ 20,300) and 358 (6,500). The nmr spectrum ($CDCl_3$) showed a broad singlet at τ 4.32 (2 H), a multiplet centered at τ 2.60 (17 H), and a singlet at τ 1.0 (1 H).

The second component was recrystallized from 95% ethanol to give 30 mg (15%) of *trans*-2-styryl-3,6-diphenylpyrazine (**14**), mp 150–151°.

Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.33; H, 5.50; N, 8.20.

The infrared spectrum (KBr) was characterized by bands at 6.13, 6.69, 6.95, 7.30, 7.82, 8.53, and 8.75 μ. The ultraviolet spectrum (95% ethanol) had maxima at 357 (ϵ 19,100), 305 (26,000), and 263 (26,000) mμ. The mass spectrum (70 eV) showed the parent ion at *m/e* 334 (base) and had prominent peaks at 333, 258, 256, 231, 230, 202, 103, and 102. The nmr spectrum ($CDCl_3$) showed a singlet at τ 1.25 (1 H) and a multiplet between τ 1.76 and 3.00 (17 H).

Oxidation of *trans*-2-Styryl-2,3-dihydro-3,6-diphenylpyrazine (14). The structure of **14** was confirmed by oxidation to **15**. A mixture of 50 mg of **14** and 45 mg of 2,3-dichloro-5,6-dicyanobenzoquinone in 50 ml of benzene was allowed to reflux for 1 hr. The solid that formed was removed by filtration and the mixture was concentrated to give a yellow oil. Preparative thick layer chromatography gave a singlet component which was recrystallized from 95% ethanol to afford a white solid (31 mg, 62%), mp 150–151°. The structure of this material was established as *trans*-2-styryl-3,6-diphenylpyrazine (**15**) by comparison with an authentic sample synthesized in the manner described below.

Preparation of *trans*-2-Styryl-3,6-diphenylpyrazine (15). To an ice-cooled solution of 1.0 g of 2,5-diphenylpyrazine in 40 ml of dry tetrahydrofuran was added 5 ml of a 2.16 *M* methyllithium solution. The reaction mixture was warmed to room temperature and stirred for 1 hr. The resulting solution was hydrolyzed with 20 ml of water and the organic layer was taken up in 100 ml of ether. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The solid which remained was collected by filtration and recrystallized from isopropyl alcohol to give 0.68 g (63%) of 2,5-diphenyl-3-methylpyrazine (**17**), mp 88–89°.

Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.70; H, 5.85; N, 11.29.

The mass spectrum exhibited the parent ion at *m/e* 246 and had major peaks at 245 (base), 115, 103, 102, and 77. The nmr spectrum ($CDCl_3$) showed a singlet at τ 7.40 (3 H), multiplets at τ 2.70 and 2.10 (10 H), and a singlet at τ 1.69 (1 H).

A mixture of 180 mg of the above 2,5-diphenyl-3-methylpyrazine, 0.2 ml of acetic anhydride, and 0.2 ml of benzaldehyde was heated at 160° in a sealed tube for 6 days. At the end of this time, the excess acetic anhydride and benzaldehyde were removed under reduced pressure and the residual solid was recrystallized from 95% ethanol to give 110 mg (44%) of *trans*-2-styryl-3,6-diphenylpyrazine (**15**), mp 149–150°. The infrared spectrum of this material was identical in all respects with that of a sample of **15** obtained from the thermolysis of **13**. A mixture melting point of the two samples was undepressed at 149–150°.

Catalytic Hydrogenation of *trans*-2-Styryl-3,6-diphenylpyrazine (15). A mixture of 100 mg of **15** in 50 ml of ethyl acetate was hydrogenated in a Parr shaker over 15 mg of 10% palladium on charcoal at 40 psig for 6 hr. The catalyst was removed by filtration and the filtrate concentrated *in vacuo* to leave a white solid. Recrystallization from 95% ethanol gave 72 mg (70%) of a colorless solid, mp 105–106°, whose structure is assigned as 2-(2-phenylethyl)-3,6-diphenylpyrazine (**18**). The infrared spectrum showed major bands at 6.70, 6.90, 7.01, 7.32, 7.41, 7.61, 8.62, 8.79, 9.15, 9.30, 10.85, 13.15, and 14.40 μ. The ultraviolet spectrum (95% ethanol) showed maxima at 258 mμ (ϵ 18,100), 309 (18,000), and a shoulder at 295 mμ. The mass spectrum (70 eV) showed the parent ion at *m/e* 336. The nmr spectrum ($CDCl_3$) shows broad singlets at τ 6.85 (4 H), 3.0 and 2.70 (15 H), and 1.08 (1 H).

Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.87; H, 6.03; N, 8.22.

Irradiation of 15 to 3,6-Diphenyl-5,6-dihydrobenzo[*f*]quinoxaline (16). A solution of 200 mg of **15** in 400 ml of benzene was irradiated for 2 hr under a nitrogen atmosphere with a 450-W Hanovia mercury arc in an immersion well apparatus fitted with a Corex filter. The solvent was removed under reduced pressure and the resulting residue was subjected to preparative thick layer chromatography. The plate was developed with a 90% benzene–10% ethyl acetate solution. Extraction of the band (R_f = 0.56) with methylene chloride followed by evaporation of the solvent gave 112 mg (56%) of a colorless solid. Recrystallization of this material from 95% ethanol gave white crystals, mp 148–149°. The structure of this material was assigned as 3,6-diphenyl-5,6-dihydrobenzo[*f*]quinoxaline (**16**) on the basis of the following data.

Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 85.81; H, 5.37; N, 8.49.

The infrared spectrum (KBr) was characterized by bands at 6.23, 6.87, 7.23, 8.32, 9.06, 9.70, 10.45, 10.90, 13.23, 14.27, and 14.45 μ. The ultraviolet spectrum (95% ethanol) showed maxima at 344 mμ (ϵ 27,100), 300 (13,900), and 287 (13,900). The mass spectrum (70 eV) showed the parent ion at *m/e* 334 and had prominent peaks at 257, 202, 127, and 126. The nmr spectrum ($CDCl_3$) showed a doublet at τ 6.51 (2 H, J = 7.5 Hz), a triplet at τ 5.62 (1 H, J = 7.5 Hz), a multiplet between τ 1.87 and 3.00 (15 H), and a singlet at τ 1.14 (1 H).

Oxidation of 16 to 3,6-Diphenylbenzo[*f*]quinoxaline (19). A mixture of 50 mg of **16** and 30 mg of 2,3-dichloro-5,6-dicyanobenzoquinone in 20 ml of xylene was allowed to reflux for 2 days. The solid that formed was removed by filtration and the filtrate was concentrated to give a dark oil. The resulting residue was subjected to preparative thick layer chromatography. The plate was developed with a 90% benzene–10% ethyl acetate solution and the band with R_f = 0.52 was extracted with methylene chloride. Evaporation of the solvent left 26 mg (52%) of 3,6-diphenylbenzo[*f*]quinoxaline (**19**), mp 190–191°.

Anal. Calcd for $C_{24}H_{16}N_2$: C, 86.72; H, 4.85; N, 8.43. Found: C, 86.40; H, 4.86; N, 8.36.

The infrared spectrum (KBr) showed bands at 6.23, 6.92, 7.15, 7.65, 8.45, 9.48, 11.26, 12.74, 13.01, 13.40, 14.18, and 14.51 μ. The ultraviolet spectrum (95% ethanol) had maxima at 293 mμ (ϵ 36,500), 253 (30,700), and 221 (34,900). The mass spectrum (70 eV) showed the parent ion at *m/e* 332 (base) and had a prominent peak at 202.

Thermolysis of 2,6,8-Triphenyl-1,5-diazabicyclo[5.1.0]octa-3,5-diene. A solution of 1.5 g of **5** in 50 ml of dry xylene was heated at reflux for 16 hr. Evaporation of the solvent under reduced pressure left an orange oil which was taken up in pentane. The first material that precipitated from the pentane solution amounted to 960 mg (64%) of a white solid. Recrystallization of this material from

cyclohexane afforded a white crystalline solid, mp 118–119°. The structure of this material is assigned as (6*S*)-3,7,8-triphenyl-1,4-diazabicyclo[4.1.1]octa-2,4-diene (**21**) on the basis of the following data.

Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.55; H, 6.00; N, 8.38.

The infrared spectrum of this material (potassium bromide pellet) is characterized by bands at 6.05, 6.23, 6.74, 6.85, 7.25, 7.75, 8.25, 8.47, 9.31, 9.74, 10.63, 10.85, 11.10, 11.92, 12.85, 13.20, 13.75, 13.95, and 14.42 μ. The ultraviolet spectrum (95% ethanol) had a maximum at 285 mμ (ϵ 21,500). The mass spectrum (70 eV) showed the parent ion at *m/e* 336 (base) and had prominent peaks at 244, 233, 206, 130, 117, 115, 104, 103, and 102. The nmr spectrum ($CDCl_3$) shows a doublet of doublets at τ 7.24 (2 H, J = 8.0 Hz, 1.5 Hz), a quartet at τ 4.35 (1 H, J = 8.0 Hz), multiplets at τ 3.42 (1 H), 3.05 (1 H), and 2.75 (15 H). When the quartet at τ 4.35 was saturated with an external field, the doublet of doublets at τ 7.24 collapsed to a broad singlet. When the multiplet at τ 3.42 was saturated, the multiplet at τ 3.05 collapsed to a doublet (J = 1.5 Hz), the quartet at τ 4.35 collapsed to a triplet, and the doublet of doublets collapsed to a doublet (J = 8 Hz). Application of an external field at τ 7.24 resulted in the collapse of the quartet at τ 4.35 to a doublet.

Further fractional crystallization of the original mother liquors afforded 170 mg (11%) of *trans*-2-styryl-3,6-diphenyl-2,3-dihydropyrazine (**14**) and 350 mg (23%) of *trans*-2-styryl-3,6-diphenylpyrazine (**15**). The identity of these products was established by comparison of spectra with the products obtained from the thermolysis of 1,4,8-triphenyl-2,5-diazaocta-1,3,5,7-tetraene (**13**).

1,3-Dipolar Cycloaddition of 2,6,8-Triphenyl-1,5-diazabicyclo-[5.1.0]octa-3,5-diene with Fumaronitrile. A 500 mg sample of **5** was dissolved in 25 ml of xylene containing 140 mg of fumaronitrile and the resulting solution was refluxed for 21 hr. The oil remaining after evaporation of the solvent was recrystallized from 95% ethanol to give 510 mg (76%) of a white solid, mp 144–145°. The crystalline solid analyzed correctly for the gross structure 2,6,10-triphenyl-8,9-dicyano-1,5-diazabicyclo[5.3.0]deca-3,5-diene (**22**).

Anal. Calcd for $C_{28}H_{22}N_4$: C, 81.13; H, 5.35; N, 13.52. Found: C, 81.00; H, 5.48; N, 13.52.

The infrared spectrum (KBr) is characterized by absorption bands at 4.48, 6.20, 6.37, 6.80, 6.91, 8.49, 8.90, 9.10, 10.36, 13.10, 13.40, and 14.41 μ. The ultraviolet spectrum (95% ethanol) had a maximum at 254 mμ (ϵ 32,800) with a shoulder at 308 (3,400) mμ. The mass spectrum (70 eV) showed the parent ion at *m/e* 414 and had prominent peaks at 336, 324, 323, 311, 284, 245, 233, 219, 182, 181, 130, and 115. The nmr spectrum (100 MHz, $CDCl_3$) showed a two proton multiplet at τ 6.69, a one proton multiplet at τ 5.98, a doublet of doublets at τ 4.87 (1 H, J = 6.0 and 4.0 Hz), a multiplet at τ 4.50 (1 H), a doublet of doublets at τ 3.98 (1 H, J = 15.5 and 5.0 Hz), a doublet at τ 3.50 (1 H, J = 15.5 Hz), and a multiplet between τ 2.06 and 2.80 (15 H).

Acid-Catalyzed Hydrolysis of 2,6,10-Triphenyl-8,9-dicyano-1,5-diazabicyclo[5.3.0]deca-3,5-diene. To a 100-mg sample of the bicycloadduct **22** in 25 ml of dioxane was added 1 ml of concentrated hydrochloric acid. The reaction mixture was allowed to stir for 1 hr at room temperature. The colored solution was diluted with 6 ml of a 1 *N* potassium hydroxide solution and extracted with ether. The ethereal layer was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the resulting residue was subjected to preparative thick layer chromatography. The plate was developed with a 90% benzene–10% ethyl acetate solution. Extraction of the upper band (R_f = 0.62) with methylene chloride followed by evaporation of the solvent gave 22 mg (70%) of cinnamaldehyde. Extraction of the lower band (R_f = 0.51) with methylene chloride gave 52 mg (70%) of *r*-2-benzoyl-*t*-3,*c*-4-dicyano-*c*-5-phenylpyrrolidine (**23**), mp 110–112°. The infrared spectrum (KBr) is characterized by bands at 3.02, 4.46, 5.94, 6.25, 6.70, 6.91, 7.67, 7.99, 8.13, 8.74, 9.88, 10.29, and 14.51 μ. The mass spectrum (70 eV) is devoid of a parent ion but shows the base peak at *m/e* 272 and a prominent peak at 196 (parent minus benzoyl group). The nmr spectrum (100 MHz, $CDCl_3$) shows a triplet at τ 6.82 (1 H, J = 9 Hz), a doublet of doublets at τ 6.20 (1 H, J = 9, 5.5 Hz), a doublet at τ 5.62 (1 H, J = 9 Hz), a doublet at τ 4.88 (1 H, J = 5.5 Hz), and a multiplet between τ 2.0 and 2.8 (10 H).

Preparation of 2-Benzoyl-4-cyano-5-phenylpyrrole by Treating 23 with Base. A mixture of 0.2 g of **23** was dissolved in 125 ml of a freshly prepared 0.4 *N* sodium methoxide–methanol solution and was allowed to reflux for 15 hr. At the end of this time the solvent was removed under reduced pressure and the light yellow oil that remained was taken up in ether, washed with water, and dried over magnesium sulfate. Evaporation of the ether left a white solid (70 mg, 35%), mp 203–204°, whose structure is assigned as 2-benzoyl-4-cyano-5-phenylpyrrole (**26**) on the basis of the following data.

Anal. Calcd for $C_{18}H_{12}N_2O$: C, 79.39; H, 4.44; N, 10.29. Found: C, 79.22; H, 4.50; N, 10.49.

The infrared spectrum (KBr) of this material is characterized by bands at 3.06, 4.50, 6.15, 6.45, 6.60, 6.82, 7.15, and 7.70 μ. The ultraviolet spectrum (95% ethanol) had maxima at 322 mμ (ϵ 23,000) and 248 (8,300). The mass spectrum (70 eV) showed the parent ion at *m/e* 272 and had prominent peaks at 243, 195, 140, 105, and 77. The nmr spectrum (100 MHz, $CDCl_3$) showed multiplets at τ 2.20 (4 H), 2.60 (6 H), and 2.90 (2 H).

1,3-Dipolar Cycloaddition of *trans*-2-Benzoyl-3-phenylaziridine with Fumaronitrile. A solution of 0.5 g of *trans*-2-benzoyl-3-phenylaziridine and 0.25 g of fumaronitrile was refluxed in 25 ml of toluene for 12 hr. The solvent was removed under reduced pressure and the residue was subjected to preparative thick layer chromatography. The plate was developed with a 90% benzene–10% ethyl acetate solution. The upper band contained 300 mg (45%) of *r*-2-benyoyl-*c*-3,*t*-4-dicyano-*t*-5-phenylpyrrolidine (**24**), mp 165–166°.

Anal. Calcd for $C_{19}H_{15}N_3O$: C, 75.73; H, 5.02; N, 13.95. Found: C, 75.76; H, 5.17; N, 13.95.

The infrared spectrum ($CDCl_3$) showed bands at 3.00, 4.46, 5.90, 6.25, 6.70, and 6.90 μ. The ultraviolet spectrum (95% ethanol) had a maximum at 247 mμ (ϵ 10,500). The mass spectrum (70 eV) showed the parent ion at *m/e* 301 and the base peak at *m/e* 196. The nmr spectrum (100 MHz, $CDCl_3$) showed a triplet at τ 6.81 (1 H, J = 8.0 Hz), a triplet at τ 6.26 (1 H, J = 8.0 Hz), a doublet at τ 5.57 (1 H, J = 8.0 Hz), a doublet at τ 4.92 (1 H, J = 8.0 Hz), and a multiplet between τ 2.1 and 2.85 (10 H).

The second component isolated from the thick layer plate, 295 mg (44%), was identified as *r*-2-benzoyl-*t*-3,*c*-4-dicyano-*t*-5-phenylpyrrolidine (**25**), mp 163–164°, on the basis of the following evidence.

Anal. Calcd for $C_{19}H_{15}N_3O$: C, 75.73; H, 5.02; N, 13.95. Found: C, 75.75; H, 4.94; N, 13.78.

The infrared spectrum was characterized by bands at 4.48, 5.90, 6.27, 6.91, 7.08, 8.08, 8.80, 9.81, 11.22, 13.20, 14.30, and 14.51 μ. The mass spectrum showed major peaks at *m/e* 272 (base), 258, 196, 195, 181, 140, 137, 105, and 77. The nmr spectrum ($CDCl_3$, 100 MHz) showed a doublet of doublets at τ 6.37 (1 H, J = 6.0, 4.0 Hz), a doublet of doublets at τ 6.26 (1 H, J = 6.0, 4.0 Hz), a doublet at τ 5.26 (1 H, J = 6.0 Hz), a doublet at τ 5.02 (1 H, J = 6.0 Hz), and a multiplet between τ 2.0 and 2.80 (10 H).

Treatment of either **24** or **25** with a sodium methoxide–methanol solution gave 2-benzoyl-4-cyano-5-phenylpyrrole (**26**) in good yield. The identity of the pyrrole was established by comparison with a sample obtained by the base treatment of **23**.

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