rated aqueous sodium chloride solution was added and the organic phase was filtered through a short column of alumina and analyzed by vpc. The ratio of dimers to **49** and **46** (ratio 3:1) was 86:14. The dienes were separated (¼ in. × 12 ft 5% squalene on Chromosorb G at 40°) and assigned stereochemistry on the basis of spectral comparisons with authentic samples. The two major dimers (ratio 1.5:1) were isolated by preparative scale vpc on a 5% SF-96 column operated at 120°: dimer **I**, *m/e* calcd, 164.1565; found, 164.1563; dimer II, *m/e* calcd, 164.1565; found, 164.1563. The first isomer exhibited the following nmr spectrum: $\delta_{TMS}^{CDCl_3}$ 5.1–5.5 (m, 6, olefinic), 2.9–3.4 (m, 2, bisallylic), 1.66 (m, 6, sp^2 CCH_3), and 1.03 (d, J = 7 Hz, 6, sp^2 CCH_3). The second dimer had a very similar spectrum: $\delta_{TMS}^{CDCl_3}$ 5.3–5.5 (m, 6), 2.5–3.0 (m, 2), 1.68 (m, 6), and 1.06 (d, J = 7 Hz, 6).

Rearrangement of 45. Exposure of **45**[23] to catalytic quantities of anhydrous silver fluoroborate as above gave a product mixture composed of *cis,trans*-2,4-hexadiene (**46**, 62%) and two dimers (ratio 1:1) in 38% yield. The nmr spectrum ($CDCl_3$) of this dimer mixture showed δ 5.25–5.55 (m, 6), 2.6–3.0 (m, 2), 1.67 (m, 6), and 1.03 (d, J = 7 Hz, 6).

Hydrogenation of the Dimers. A mixture of dimers (7.9 mg) was hydrogenated in 2 ml of ethyl acetate over 15 mg of 10% palladium on carbon at room temperature and atmospheric pressure. The processed solution was freed of solvent by preparative vpc (¼ in. × 20 ft 5% QF-1 on Chromosorb G at 130°). There was obtained 7.3 mg of 4,7-dimethyldecane which was identical in all respects with the authentic sample prepared below.

4,7-Dimethyldecane. A solution of 3.00 g (0.015 mol) of 4,7-dimethyl-5-decyne-4,7-diol (K&K Laboratories) in 40 ml of absoute ethanol containing 150 mg of 10% palladium on carbon was hydrogenated in a Parr apparatus at 50 psig. After 20.5 hr, the catalyst was separated by filtration and the solvent was removed by distillation through a short Vigreux column. The hydrocarbon product was separated from residual hydroxylic material by vpc isolation as above: *m/e* calcd, 170.2034; found, 170.2032.

Acknowledgment. Partial support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Photochemical Reorganizations in the 1,3-Diazabicyclo[3.1.0]hex-3-ene System[1]

Albert Padwa*[2] and Edward Glazer

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received March 21, 1972*

Abstract: The irradiation of a triaryl-substituted 1,3-diazabicyclo[3.1.0]hex-3-ene in benzene results in ring opening to an enediimine intermediate which undergoes subsequent thermal disrotatory closure to a *cis*-dihydropyrazine. The same enediimine intermediate was formed on irradiation of a *cis*- or *trans*-dihydropyrazine. An intriguing variation of the normal reaction pathway occurs when the irradiation is carried out in an alcoholic medium. Photolysis of *endo*- or *exo*-2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**5** and **6**, respectively) in methanol gave 2,4-diphenyl-1-methoxybenzylimidazoline (**25**). The photoreaction can be formulated as proceeding *via* an azomethine ylide by cleavage of the aziridine C–C bond. The azomethine ylide will lead to imidazoline **25** by addition of methanol. Irradiation of **5** or **6** in an ethanol glass produced a bright red color which was rapidly discharged by the addition of dimethyl acetylenedicarboxylate. The formation of a cycloadduct supports the postulate that the photochemistry of the diazabicyclo ring proceeds *via* the formation of an azomethine ylide which subsequently opens to an enediimine.

Light-induced transformations of cyclic dienes have been the subject of recent intensive study.[3,4] Derivatives of 1,3-cyclohexadiene, for example, have been transformed into a vast array of photoproducts *via* ring-opening processes,[5] valence-bond tautomerism reactions,[6] bond switching mechanisms,[7] and dimerization pathways.[8] Despite the fact that photochemical isomerizations of cyclic dienes have been well documented, investigation of suitable heterocyclic analogs in light-induced reactions has been somewhat limited,[9,10] even though the generality of the photochemical ring-opening reactions for systems isoelectronic with 1,3-cyclohexadienes was predicted by Barton 13 years ago.[11] One exception is the work of Beak and Miesel who reported the ready photoisomerization of 2,3-dialkyl-2,3-dihydropyrazines (**1**) to sub-

(1) Photochemical Transformations of Small Ring Heterocyclic Compounds. XLII. For part XLI, see A. Padwa, L. Brodsky, and S. Clough, *J. Amer. Chem. Soc.*, **94**, 6767 (1972).

(2) Alfred P. Sloan Foundation Fellow, 1968–1972, and National Institutes of Health Special Postdoctoral Fellow, 1972.

(3) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

(4) G. J. Fonken in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 222.

(5) (a) D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960); (b) P. de Mayo and S. T. Reid, *Quart. Rev., Chem. Soc.*, **15**, 393 (1961); (c) E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 146 (1961); (d) E. Havinga, *Chimia*, **16**, 146 (1962); (e) R. L. Autrey, D. H. R. Barton, A. K. Ganguly, and W. H, Reusch, *J. Chem. Soc.*, 3313 (1961); (f) R. Srinivason, *J. Chem. Phys.*, **38**, 1039 (1963); (g) G. J. Fonken and K. Mehrotra, *Chem. Ind. (London)*, 1025 (1964); (h) W. G. Dauben and R. M. Coates, *J. Org. Chem.*, **29**, 2761 (1964); (i) J. Meinwald and P. H. Mazzochi, *J. Amer. Chem. Soc.*, **88**, 2851 (1966).

(6) (a) W. G. Dauben and R. M. Coates, *ibid.*, **86**, 2490 (1964); (b) H. Prinzbach and J. H. Hartenstein, *Angew. Chem.*, 74, 651 (1962); 75, 639 (1963); E. E. van Tamelen, S. P. Pappas, and K. L. Kirk, *J. Amer. Chem. Soc.*, **93**, 6092 (1971).

(7) (a) D. H. R. Barton and A. S. Kende, *J. Chem. Soc.*, **688** (1958); (b) W. G. Dauben and G. J. Fonken, *J. Amer. Chem. Soc.*, **81**, 4060 (1959); (c) D. H. R. Barton, R. Bernasconi, and J. Klein, *J. Chem. Soc.*, 511 (1960); (d) G. R. Evanega, W. Bergmann, and J. English, Jr., *J. Org. Chem.*, **27**, 13 (1962); (e) H. Hart and A. J. Waring, *Tetrahedron Lett.*, 325 (1965); (f) M. Pomerantz and G. W. Gruber, *J. Amer. Chem. Soc.*, **93**, 6615 (1971); (g) J. Meinwald and P. H. Mazzocchi, *ibid.*, **89**, 696 (1967).

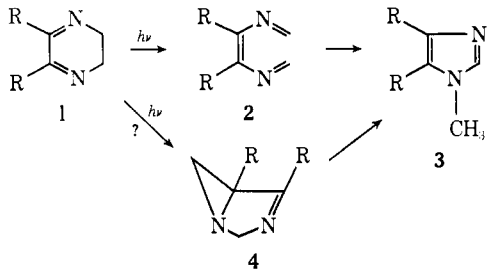
(8) (a) L. A. Paquette and G. Slomp, *ibid.*, **85**, 765 (1963); (b) E. C. Taylor, R. O. Kan, and W. W. Paudler, *ibid.*, **85**, 776 (1963).

(9) D. R. Arnold, V. Y. Abraitys, and D. Mcleod, Jr., *Can. J. Chem.*, **49**, 823 (1971).

(10) P. Beak and W. R. Messer in "Organic Photochemistry," Vol. II, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1969, p 117.

(11) D. H. R. Barton, *Helv. Chim. Acta*, 42, 2604 (1959).

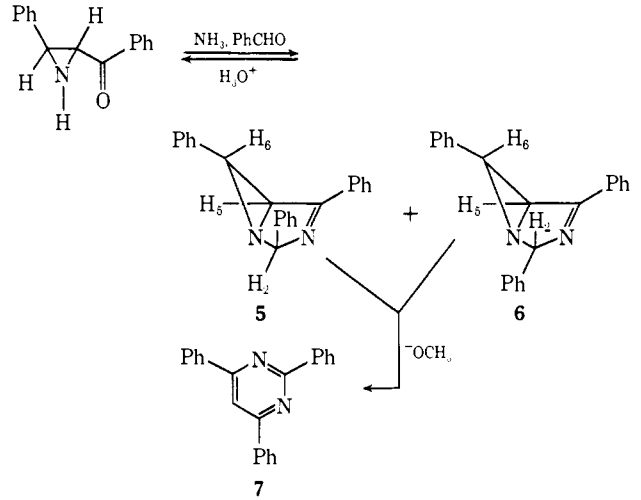
stituted imidazoles[12] (**3**). The reaction was suggested to proceed *via* an irreversibly formed enediimine intermediate **2** which underwent subsequent ring closure to **3**. While intermediate **2** was not detected, the imidazole and the other side products produced made this mechanism quite plausible.



With a desire to discover new photochemical pathways of appropriate heterocycles, we have examined the irradiation of the 1,3-diazabicyclo[3.1.0]hex-3-ene ring system **4**.[13] This study was of interest for several reasons. First, a 1,3-diazabicyclohexene **4** could fulfill the function of **2** in the photorearrangement of 2,3-dihydropyrazines **1** to imidazoles **3**. The photorearrangement of **1** to **4** is not unreasonable since, in at least one case, a 1,3-cyclohexadiene has been shown to be the direct precursor of the bicyclo[3.1.0]hex-2-ene system.[14] It seemed plausible that a system such as **4** upon irradiation could give rise to an imidazole. Secondly, and perhaps of greater significance, is that **4** bears the same formal resemblance to bicyclo[3.1.0]-hex-2-ene that 2,3-dihydropyrazine does to 1,3-cyclohexadiene. A comparison of the photochemistry of a 1,3-diazabicyclohexene with its carbocyclic counterpart could be of practical and theoretical interest. The influence of substituents on the stereochemical course of 1,3-cyclohexadienes to bicyclo[3.1.0]hex-2-enes has recently been reported from this laboratory.[15] Analogy with the carbocyclic system suggests the possible applicability of the Woodward–Hoffmann orbital symmetry rules in the photochemistry of the diazabicyclic system.[16] Thirdly, reactions involving the photochemical cleavage of aziridines to azomethine ylides and their subsequent 1,3-dipolar additions to reactive carbon–carbon multiple bonds are well known.[17–21] Should the photochemistry of **4** proceed by cleavage of the aziridine C–C bond,[22] then it should be possible to trap the 1,3-dipolar intermediate by cycloaddition with a reactive dipolarophile. This paper describes some of the interesting features that were encountered in our study of the photochemistry of *exo*- and *endo*-triaryl-1,3- diazabicyclo[3.1.0]hex-3-enes.

Results and Discussion

endo- and *exo*-2,4,6-triphenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene (**5** and **6**) were prepared by treating *trans*-2-phenyl-3-benzoylaziridine with benzaldehyde in an ethanolic solution saturated with ammonia and containing small quantities of ammonium bromide.[23]



Fractional crystallization gave **5**, mp 143–144°, and **6**, mp 154–155°. Spectral data and elemental analyses were in complete agreement with the structures and are summarized in the Experimental Section. The stereochemistry of the individual isomers could be readily discerned by examination of their nmr spectra. The appearance of proton H_2 in **6** (τ 3.75) at high field relative to proton H_2 in **5** is compatible with the anisotropic shielding of this proton by the adjacent aziridine ring.[24] In addition, the location of proton H_6 at a higher field (τ 7.50) in compound **5** relative to **6** (τ 7.30) is consistent with the expected shielding effect of the neighboring phenyl ring.[25] The exo stereochemistry of **6** was further strengthened by the fact that it showed a strong intramolecular nuclear Overhauser

(12) P. Beak and J. L. Miesel, *J. Amer. Chem. Soc.*, **89**, 2375 (1967).

(13) For a preliminary report of this work, see A. Padwa, S. Clough, and E. Glazer, *ibid.*, **92**, 1778 (1970); *Chem. Commun.*, **838** (1971).

(14) E. F. Ullman, W. A. Henderson, Jr., and K. R. Huffman, *Tetrahedron Lett.*, 935 (1967).

(15) A. Padwa, L. Brodsky, and S. Clough, *Chem. Commun.*, 417 (1971).

(16) R. B. Woodward and R. Hoffman, *Angew Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(17) H. W. Heine and R. Peavy, *Tetrahedron Lett.*, 3123 (1965); *J. Org. Chem.*, **31**, 3924 (1966); H. W. Heine, A. B. Smith, and J. D. Bower, *ibid.*, **33**, 1097 (1968).

(18) A. Padwa and L. Hamilton, *Tetrahedron Lett.*, 4363 (1965); A. Padwa and W. Eisenhardt, *Chem. Commun.*, 380 (1968); A. Padwa, L. Gehrlein, and S. Clough, *ibid.*, 74 (1972).

(19) 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).

(20) J. W. Lown, G. Dallas, and T. W. Maloney, *Can. J. Chem.*, **47**, 3557 (1969); *ibid.*, 4335 (1969); *Chem. Commun.*, 1543 (1968); 247 (1971); J. W. Lown, *Rec. Chem. Progr.*, **32**, 51 (1971).

(21) P. B. Woller and N. H. Cromwell, *J. Heterocycl. Chem.*, **5**, 579 (1968); *J. Org. Chem.*, **35**, 888 (1970).

(22) After our initial publication in this area,[13] Trozzolo and DoMinh have presented evidence demonstrating the formation of an azomethine ylide from the irradiation of the diazabicyclic system: T. DoMinh and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **92**, 6997 (1970); **94**, 4046 (1972).

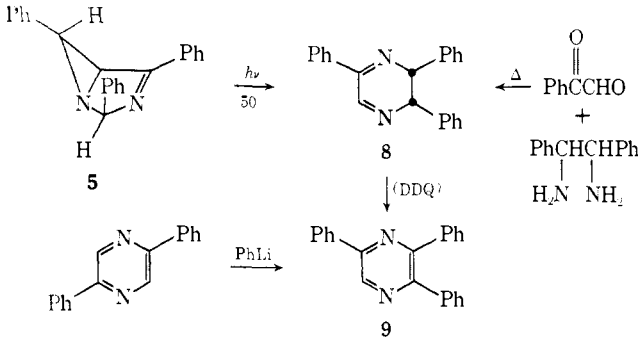
(23) H. Heine, R. Weese, R. Cooper, and A. Durbetaki, *J. Org. Chem.*, **32**, 2708 (1967). These authors were the first to synthesize the diazabicyclo[3.1.0]hex-3-ene system. They report only the formation of **6** from the above reaction.

(24) K. Tosi, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Lett.*, 869 (1965).

(25) (a) One additional structure which was considered for compound **5** was 2-*exo*-6-*endo*-2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene. This structure was eliminated on the basis of the following considerations. (1) Acid-catalyzed hydrolysis of **5** afforded only *trans*-2-phenyl-3-benzoylaziridine. (2) Proton H_2 for this structure would be expected to be at higher chemical field than proton H_2 in **6** due to the shielding effect of both the phenyl group and aziridine ring. This is not the case. (3) Also, the coupling constants for the vicinal C_5 and C_6 protons are consistent with the trans configuration. If these protons were cis, a coupling constant larger than 3 Hz should have been observed.[25b,c] (b) K. Tori, T. Komeno, and T. Nakagawa, *J. Org. Chem.*, **29**, 1136 (1964); (c) J. L. Pierre, P. Chautemps, and P. Arnaud, *C. R. Acad. Sci.*, **261**, 4025 (1965).

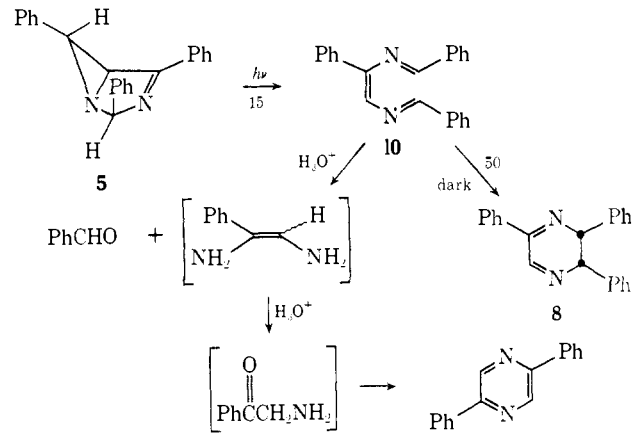
effect[26] (NOE). In the nmr spectrum of **6**, application of an intense radiofrequency field at the transition energy of proton H_2 produced a NOE at proton H_6 (31% intensity increase), whereas similar irradiation of the H_2 proton in the other isomer had no effect. Accordingly, protons H_2 and H_6 in **6** must be proximal, an observation which requires the spatial relationship embodied uniquely in the exo isomer. The trans relationship of protons H_5 and H_6 was established by the acid-catalyzed hydrolysis of **5** (and **6**) to *trans*-2-phenyl-3-benzoylaziridine.[23] Both diazabicyclohexenes were found to undergo oxidative rearrangement to 2,4,6-triphenylpyrimidine (**7**) when treated with methanolic sodium methoxide.[23]

Irradiation of a solution of **5** in benzene at 50° in a Pyrex immersion apparatus with a 450-W Hanovia lamp for 4 hr led to complete disappearance of starting material. Conventional isolation procedures afforded 94% of a solid, mp 145–146°, whose structure is assigned as *cis*-2,3-dihydro-2,3,5-triphenylpyrazine (**8**). Chemical confirmation was obtained by the oxidation of **8** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to 2,3,5-triphenylpyrazine (**9**). An authentic sample of **9** was prepared by treating 2,5-diphenylpyrazine with phenyllithium according to established procedures.[27,28] Structure **8** was further confirmed by its unequivocal synthesis from phenylglyoxal and *meso*-stilbenediamine.

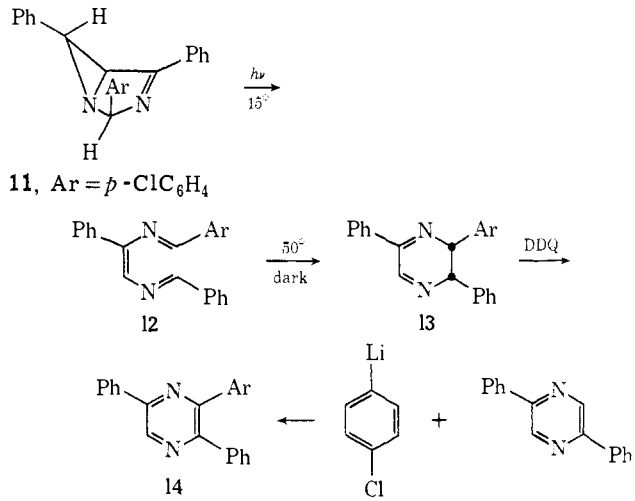


Irradiation of a solution of **5** at 15° for the same period gave virtually no dihydropyrazine **8**. Instead, formation of a new product occurred. At 50°, thermal rearrangement of the labile photoproduct took place. These reactions are reproducible and clearly require that some photochemically generated precursor of **8** persists after the light source is extinguished which then rearranges upon heating (in the dark) to *cis*-dihydropyrazine **8**. From its absorption spectra [ir 6.14 μ; uv λ_{max} 360 nm (ϵ 12,000); nmr τ 2.50 (m, 16 H) and 1.50 (s, 2 H)], its thermal instability, and behavior on hydrolysis (*i.e.*, formation of 2,5-diphenylpyrazine and benzaldehyde), this compound is most reasonably assigned enediimine structure **10**.

The validity of the reaction sequence advanced to account for the formation of *cis*-dihydropyrazine **8** is further supported by studying the photochemistry of *endo*-2-*p*-chlorophenyl- 4,6- diphenyl- 1,3- diazabicyclo-[3.1.0]hex-3-ene (**11**). This compound was readily prepared by the reaction of *trans*-2-benzoyl-3-phenylaziridine with *p*-chlorobenzaldehyde and ammonia and



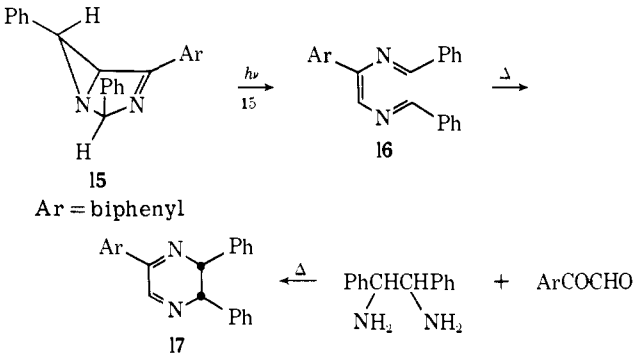
provides a convenient label at the 2 position of the diazabicyclic ring system. Irradiation of **11** in benzene at 15° through Pyrex filters resulted in the formation of a single photoproduct **12**. The physical and chemical data confirm the identity of the photoproduct as 1-*p*-chlorophenyl-3,6-diphenyl-2,5-diaza-1,3,5-hexatriene (**12**). Heating a benzene solution of **12** in the dark at 50° resulted in the formation of *cis*-2,3-dihydro-2,5-diphenyl-3-*p*-chlorophenylpyrazine (**13**), mp 125–126°. The structure of dihydropyrazine **13** was established by oxidation to 2,5-diphenyl-3-*p*-chlorophenylpyrazine (**14**). Structure **14** was independently synthesized by treating 2,5-diphenylpyrazine with *p*-chlorophenyllithium.



Further indication of the generality of the photochemical ring-opening reaction comes from the observation that *endo*-2,6-diphenyl-4-(4′-phenyl)phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**15**) gave enediimine **16** as a crystalline solid (98%) on irradiation. Heating **16** at 50° resulted in the formation of *cis*-2,3-dihydro-2,3-diphenyl-5- (4′-phenyl) phenylpyrazine (**17**). The structure of **17** was established by spectral and physical comparison with an authentic sample.

According to orbital symmetry considerations, ring opening of an electronically excited 2-*endo*-6-*exo*-disubstituted bicyclo[3.1.0]hex-2-ene (such as **5**, **11**, or **15**) to a *trans,cis,trans*-hexatriene is an allowed process.[16] Orbital symmetry also predicts that the hexatriene should undergo thermal ring closure by disrotatory motion. The formation of only *cis*-dihydropyrazines from the irradiation of *endo*-diazabicyclohexenes **5**, **11**,

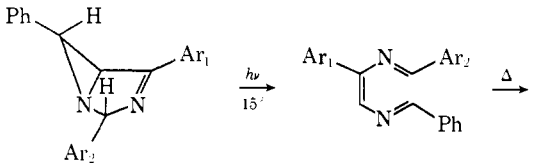
(26) For a recent review, see G. Moreau, *Bull. Soc. Chim. Fr.*, 1770 (1969).
(27) B. Klein and P. Sperri, *J. Amer. Chem. Soc.*, 73, 2949 (1951).
(28) H. Gilman, W. Langham, and F. Moore, *ibid.*, 62, 2327 (1940).



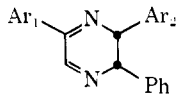
15

Ar = biphenyl

and **15** is thus in accord with the Woodward–Hoffmann rules. It should be emphasized that although orbital symmetry control is implicated, the results do not necessarily prove such control because several geometries of uncertain reactivity are available to the enediimine intermediate. Also, as will be shown later, the ring-opening reaction actually proceeds in a stepwise manner *via* the formation of a discrete 1,3-dipolar intermediate. In order to determine whether the reactions encountered with the diazabicyclohexene system are consistent with orbital symmetry interpretations, we have investigated the photochemistry of *exo*-diazabicyclohexenes **6**, **18**, and **19**. Formation of a *trans*-2,3-dihydropyrazine from these substituted 2-exo bicyclic systems was expected on the basis of orbital symmetry considerations. We found, however, that irradiation of **6** at 50° resulted in the exclusive formation of *cis*-dihydropyrazine **8**. Similar irradiation of **18** and **19** gave *cis*-dihydropyrazines **13** and **17** with no detectable amounts of the isomeric *trans*-dihydropyrazines.

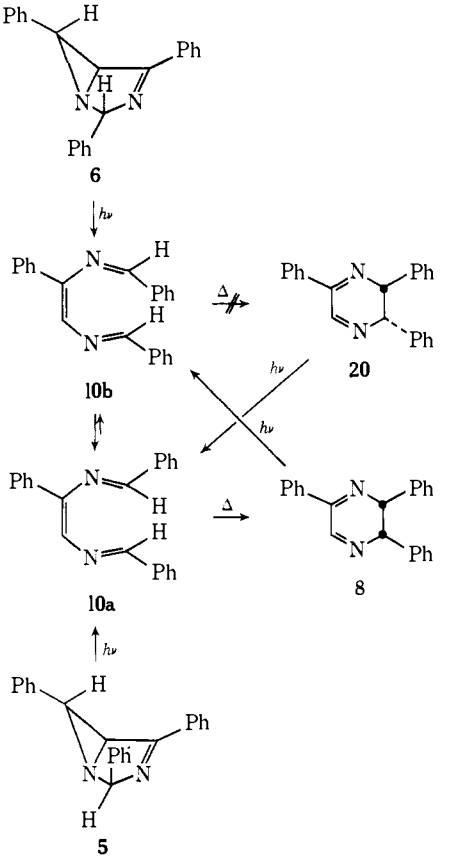


5, $Ar_1 = Ar_2 = Ph$
18, $Ar_1 = Ph$; $Ar_2 = p\text{-}ClC_6H_4$
19, Ar_1 = biphenyl; $Ar_2 = Ph$



8, $Ar_1 = Ar_2 = Ph$
13, $Ar_1 = Ph$; $Ar_2 = p\text{-}ClC_6H_4$
17, Ar_1 = biphenyl; $Ar_2 = Ph$

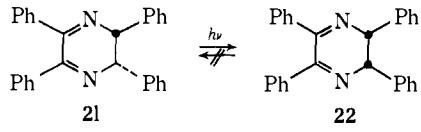
One explanation to account for the above results is that the enediimine exists as an equilibrium mixture of two isomers, **10a** and **10b**, the more prevalent isomer being **10a**. The first step would then involve ring opening of **6** to an enediimine **10b**. The second step of the reaction could be pictured as involving syn–anti isomerization of **10b** to **10a** which would then undergo thermal disrotatory closure to give **8**. Syn–anti isomerizations of *N*-arylimines are known to occur rapidly[29,30] and provide reasonable chemical analogy for the second step. The syn–anti isomerization mechanism supported by most workers is the inversion or "lateral shift mechanism," in which the isomerization proceeds through a linear transition state in which the lone pair on nitrogen has rehybridized to a p orbital.[31–35]



In support of the suggested mechanism we find that irradiation of *trans*-dihydropyrazine **20** at 15° gives a labile enediimine which thermally cyclizes to give **8**. On the other hand, irradiation of *cis*-dihydropyrazine **8** at 15° affords an enediimine which regenerates starting material on warming. These results indicate that **10a** is an important intermediate in the isomerization of **20** to **8** and that irradiation of **8** results in conrotatory opening to give **10b** which rapidly isomerizes to **10a**. A similar photoisomerization was found to occur with the 2,3-dihydro-2,3,5,6-tetraphenylpyrazine system. Exposure of *trans*-dihydropyrazine **21** to uv light gave rise to *cis*-dihydropyrazine **22**. Similar irradiation of **22** resulted in recovered starting material. The exclusive formation of **22** from **21** is again compatible with the intervention of an enediimine intermediate which undergoes thermal disrotatory cyclization.

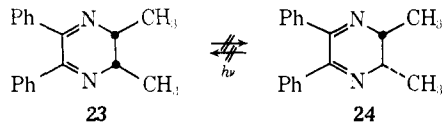
As was mentioned earlier, Beak and Miesel report that 2,3-dialkyl-2,3-dihydropyrazines rearrange to imidazoles upon irradiation.[12] These authors suggest that

(29) D. Y. Curtin and J. W. Hauser, *ibid.*, 83, 3474 (1961).
(30) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *ibid.*, 88, 2775 (1966).
(31) (a) H. Kessler, *Angew. Chem.*, 80, 971 (1968); *Angew. Chem., Int. Ed. Engl.*, 7, 898 (1968); (b) H. Kessler, *Tetrahedron Lett.*, 2041 (1968); (c) H. Kessler and D. Leibfritz, *Tetrahedron*, 25, 5127 (1969); *Tetrahedron Lett.*, 1423 (1970).
(32) E. A. Jeffery, A. Meisters, and T. Mole, *Tetrahedron*, 25, 741 (1969).
(33) C. G, McCarty and D. M. Wieland, *Tetrahedron Lett.*, 1787 (1969).
(34) F. Vogtle, A. Mannschreck, and H. A. Staab, *Justus Liebigs Ann. Chem.*, 708, 51 (1967); H. A. Staab, F. Vogtle, and A. Mannschreck, *Tetrahedron Lett.*, 697 (1965).
(35) M. Raban and E. Carlson, *J. Amer. Chem. Soc.*, 93, 685 (1971).



21 22

the reaction proceeds through an irreversibly formed enediimine intermediate. This conclusion was based on the fact that racemization did not occur on photolysis of an optically active dihydropyrazine.[12] Consistent with this explanation is the absence of photochemical interconversion of the cis (**23**) and trans (**24**) isomers of 2,3-dihydro-2,3-dimethyl-5,6-diphenylpyrazine.[36] It is interesting to note that we do not detect



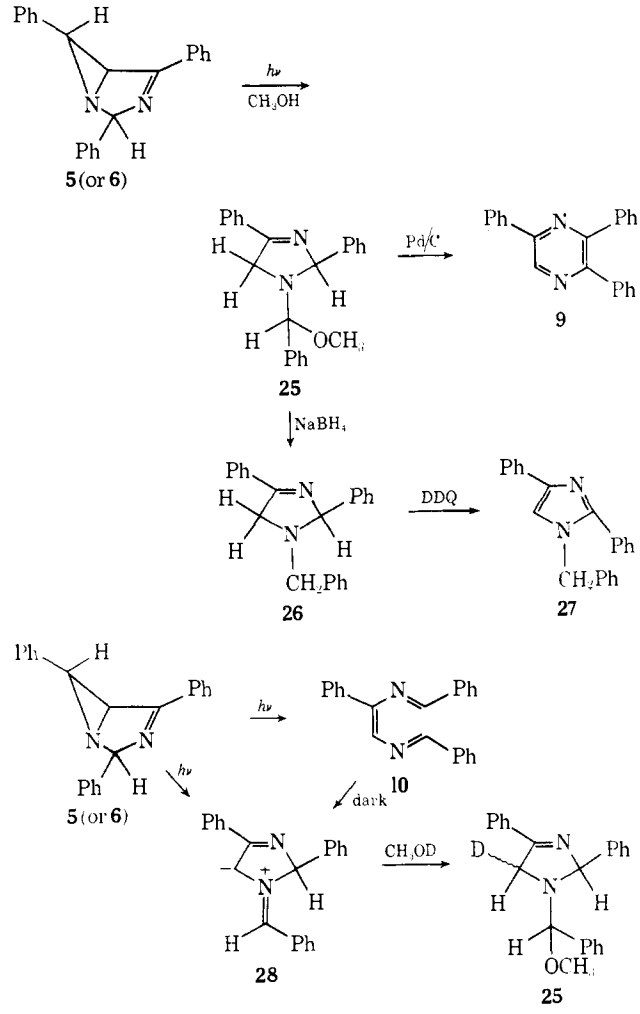
23 24

any imidazoles in our systems (benzene solvent) and that isomerization of *trans*- to *cis*-dihydropyrazine does occur (*i.e.*, **20** → **8** and **21** → **22**). In order to resolve this apparent anomaly, we have studied the photochemistry of both the diazabicyclic and dihydropyrazine systems in an alcoholic medium, since this was the solvent system employed by Beak and Miesel. Our results indicate that an intriguing variation of the normal reaction pathway occurs when the irradiation is carried out in methanol.

When a dilute solution of *exo*- or *endo*-diazabicyclohexene **5** (or **6**) in methanol was irradiated through a Pyrex filter, the major product formed (60%) was identified as 2,4-diphenyl-1-methoxybenzylimidazoline (**25**). Under these conditions no dihydropyrazine (**8** or **20**) was formed. The structure of **25** was characterized by its spectral data, in particular, the nmr spectrum which showed a singlet at τ 6.70 (3 H), a doublet of doublets at τ 6.15 (J = 14 and 5.0 Hz, 1 H), a doublet of doublets at τ 5.62 (J = 14 and 5.0 Hz, 1 H), a singlet at τ 5.07 (1 H), a triplet at τ 3.80 (J = 5.0 Hz, 1 H), and a multiplet at τ 2.60 (15 H). Chemical confirmation was obtained by the oxidation of **25** with palladium on charcoal to 2,3,5-triphenylpyrazine. Structure **25** was further confirmed by sodium borohydride reduction to *N*-benzyl-2,4-diphenylimidazoline (**26**), mp 89–90°, followed by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to *N*-benzyl-2,4-diphenylimidazole (**27**), mp 122–124°.

The photoconversion of **5** (or **6**) to imidazoline **25** may be formulated as proceeding *via* enediimine **10** which undergoes ground-state ring closure by intramolecular nucleophilic addition at the imine carbon atom to give intermediate **28** which leads to imidazoline **25** by addition of methanol. The cyclization of **10** to **28** as a nonphotochemical reaction has reasonable chemical precedent.[37] Alternatively, it could be argued that the reaction proceeds *via* the formation of azomethine ylide **28** by cleavage of the aziridine C–C bond[22] prior to the formation of enediimine **10**.

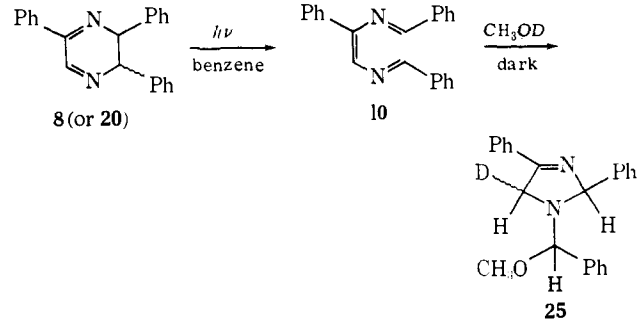
Support for the proposed intermediate **28** is provided by the deuterium incorporation observed in the course of the photolysis. Irradiation of **5** (or **6**) in



5 (or 6) 25 9 25 26 27 5 (or 6) 10 28 25

deuteriomethanol gave imidazoline **25**-d_1. The extent of deuterium incorporation was determined by mass spectrometry, and the position of deuteration was determined by nmr analysis. The incorporation of a single deuterium atom in the 5 position (50% trans–50% cis) of the product imidazoline is expected for an intermediate corresponding to **28** in this reaction.

Further support for this sequence was obtained by generation of enediimine **10** by irradiating *cis*- or *trans*-2,3-dihydro-2,3-5-triphenylpyrazine (**8** or **20**) in benzene. Removal of the solvent followed by addition of methanol (in the dark) gave imidazoline **25**.



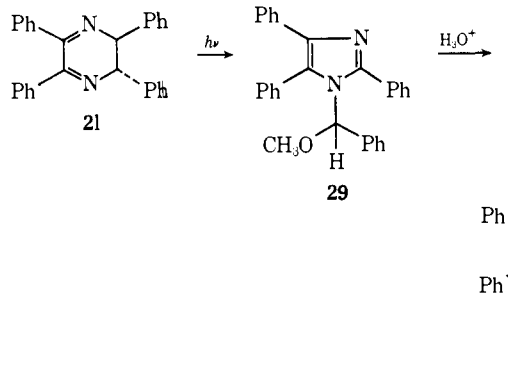
8 (or 20) 10 25

Similar irradiation of *trans*-2,3-dihydro-2,3,5,6-tetraphenylpyrazine (**21**) in methanol resulted in the isolation of two products. The major product (mp 170–172°, 62%) was identified as 1-methoxybenzyl-2,3,5-triphenylimidazole (**29**) on the basis of the physical (see Experimental Section) and chemical data. This

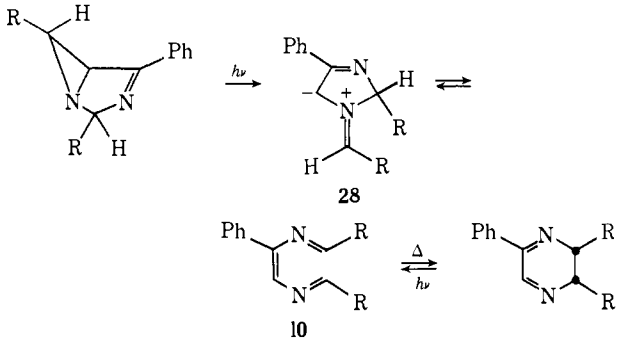
(36) We have found that irradiation of 23 or 24 in cyclohexane gave *N*-vinyl-2-methyl-4,5-diphenylimidazole with no detectable trans–cis interconversion of isomers: see A. Padwa, J. Smolanoff, and S. I. Wetmore, Jr., *Chem. Commun.*, 409 (1972).

(37) G. McCoy and A. Day, *J. Amer. Chem. Soc.*, **65**, 2159 (1943).

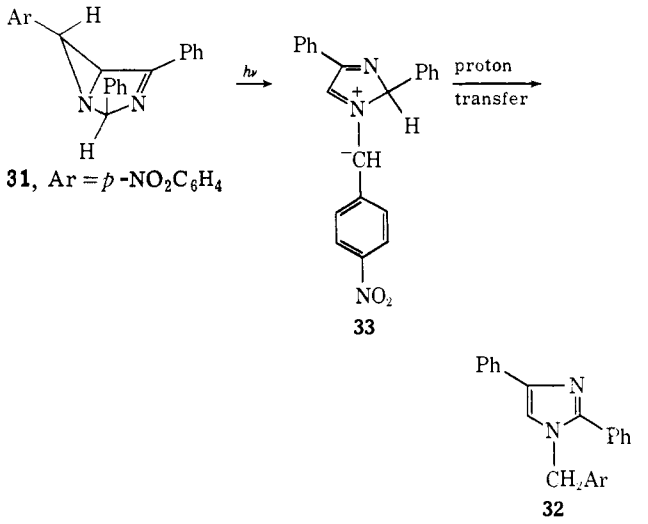
structure was confirmed by acid hydrolysis to the known 2,3,5-triphenylimidazole **30**. Imidazole **30** was identified as the minor component in the crude reaction mixture. Under these conditions no detectable quantities of *cis*-dihydropyrazine **22** were found.



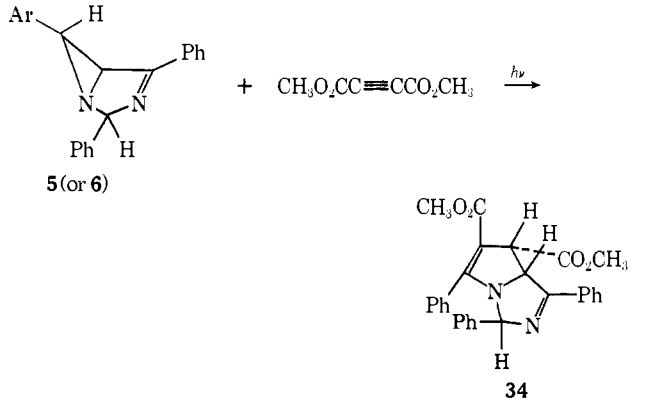
Our inability to isolate *cis*-dihydropyrazine **22** from the irradiation of **21** in methanol demonstrates that the direction of cyclization of the enediimine intermediate is sensitive to both the nature of the solvent and the substituent groups. In nonpolar solvents such as benzene (or cyclohexane), electrocyclization is the preferred pathway. A different mode of cyclization occurs when polar solvents such as methanol are used. This involves nucleophilic attack of nitrogen on the neighboring imine carbon atom and formation of the same azomethine ylide that is produced upon irradiation of the diazabicyclo[3.1.0]hex-3-ene system. This mode of cyclization is undoubtedly related to the ability of methanol to solvate the developing charges. The electrocyclic ring closure of the triarylenediimine intermediate back to the dihydropyrazine system in nonpolar solvents occurs to the exclusion of imidazole formation. This may be the result of the decreased electrophilicity of the imine carbon toward nucleophilic attack when the imine moiety bears a phenyl group. It is interesting to note that we do not detect the presence of a diazabicyclohexene when the irradiation of a dihydropyrazine is carried out in a nonpolar solvent. This would imply that the equilibrium, **10** $\rightleftarrows$ **28**, is almost totally on the side of **10** in nonpolar solvents. The direct ring opening of the 1,3-diazabicyclo[3.1.0]hex-3-ene to the 1,3-dipole **28** will be discussed below.



Irradiation of *endo*-6-*p*-nitrophenyl-2,4-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**31**) in methanol proceeded by a slightly different path and produced 1-*p*-nitrobenzyl-2,4-diphenylimidazole (**32**). This structure was verified by an independent synthesis from *p*-nitrobenzyl bromide and 2,4-diphenylimidazole. The formation of **32** may be rationalized as proceeding *via* cleavage of the C–C bond of the aziridine ring to generate azomethine ylide **33**. In this case, because of the *p*-nitrophenyl substituent, the charge distribution in the zwitterion is opposite that pictured previously. Zwitterion **33** will readily lead to the observed product by a proton transfer.



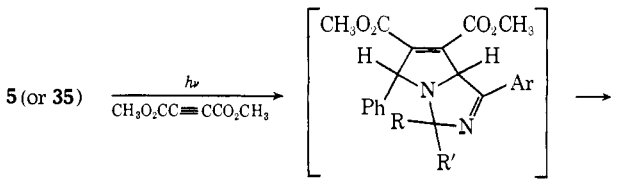
During the course of our photochemical studies, we noticed that the diazabicyclic compounds developed a slight red tinge of color on standing in the solid form at room temperature. Intensely colored material could be developed by irradiation of the solid in a frozen glass at 77°K. The nature of the colored intermediate was established by trapping experiments. Irradiation of a mixture of **5** (or **6**) and dimethyl acetylenedicarboxylate in an ethanol glass at 77°K produced a bright red color which was readily discharged on warming to give a single cycloproduct. The structure of the adduct was assigned as dimethyl (3*R**,7*R**,7a*S**)-7,7a-dihydro-1,3,5-triphenyl-3*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (**34**) on the basis of its uv, ir, mass spectral, and nmr data: mp 123–124°; nmr (pyridine-d_5) singlets at τ 6.62 (3 H) and 6.58 (3 H), doublets at τ 4.54 (1 H, J = 4.0 Hz), 3.80 (1 H, J = 4.0 Hz), and a triplet at τ 3.62 (1 H, J = 4.0 Hz). The stereochemical assignment rests on the magnitude of the coupling constants and their relationship to appropriate model systems.[2,38,39]



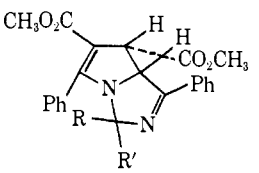
While our studies were in progress there appeared a report by Trozzolo and DoMinh on the photochemistry

(38) A. Padwa and L. Hamilton, *J. Heterocycl. Chem.*, 4, 118 (1967).
(39) H. W. Heine and R. P. Hanzel, *J. Org. Chem.*, 34, 171 (1969).

of the related 2,2-dimethyl-4-phenyl-6-*p*-nitrophenyl-1,-3-diazabicyclo[3.1.0]hex-3-ene (**35**).[22] These workers found that irradiation of **35** in an ethanol glass at liquid nitrogen temperature produced a bright red colored intermediate which could be trapped by cycloaddition with added dipolarophiles. The structure of the cycloadduct **34** obtained from **5** and dimethyl acetylenedicarboxylate is structurally related to the adduct **37** isolated by Trozzolo and DoMinh. Both



36



34, Ar = R = Ph; R′ = H
37, Ar = *p*-$NO_2C_6H_4$; R = R′ = CH_3

cycloadditions presumably proceed by way of a transient Δ^3-pyrroline intermediate (*i.e.*, **36**) which undergoes a subsequent 1,3-suprafacial hydrogen shift.[40]

When a solution of **5** (or **6**) and dimethyl acetylenedicarboxylate was irradiated for 2.5 hr, no red coloration was observed and adduct **34** was isolated in good yield (72%). It is noteworthy that no detectable quantities of *cis*-dihydropyrazine **8** were formed under the conditions of irradiation. These results strongly suggest that the opening of the diazabicyclic ring occurs in a stepwise fashion *via* an azomethine ylide intermediate **28** which subsequently opens to enediimine **10**.

Experimental Section[41]

***endo*- and *exo*-2,4,6-Triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (5 and 6).** A solution containing 5.0 g of *trans*-2-benzoyl-3-phenylaziridine,[42] 0.5 g of ammonium bromide, and 15 ml of benzaldehyde in 100 ml of ethanol was saturated with ammonia at 0°. The solution was allowed to stand at room temperature for 3 days, at which time a crystalline precipitate formed. Fractional crystallization of the crude solid from 95% ethanol gave 2.8 g (42%) of *endo*-2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**5**), mp 143–144°.

Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85; H, 9.03. Found: C, 84.96; H, 5.84; N, 9.04.

The infrared spectrum (KBr) showed bands at 6.10, 6.69, 6.90, 9.55, 9.75, 12.90, 13.35, 13.60, 14.30, and 14.50 μ. The ultraviolet spectrum (95% ethanol) has a maximum at 245 nm (ε 20,000). The 60-MHz nmr spectrum ($CDCl_3$) shows a doublet of doublets at τ 7.50 (1 H, *J* = 2.5 and 1.3 Hz), a triplet at τ 6.25 (1 H, *J* = 2.5 Hz), a broad singlet at τ 3.08 (1 H), and a multiplet at τ 1.75–2.75 (15 H). The mass spectrum (70 eV) shows the molecular ion at *m/e* 310 and has other major peaks at 309, 308 (base), 307, 103, and 102 mass units.

The filtrate was allowed to stand for several days at which time 1.4 g (21%) of *exo*-2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (6) precipitated, mp 154–155° (lit.[23] 153–154°).

***endo*- and *exo*-2-*p*-Chlorophenyl-4,6-diphenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene (11 and 18).** A solution containing 1.0 g of 2-benzoyl-3-phenylaziridine, 2.5 g of *p*-chlorobenzaldehyde, and 0.1 g of ammonium bromide in 20 ml of absolute ethanol was saturated with ammonia at 0°. The solution was allowed to stand at room temperature for 5 days and the solvent was removed *in vacuo* to give a solid. Fractional crystallization of this material from 95% ethanol gave a colorless solid (0.68 g, 40%), mp 142–143°, whose structure is assigned as *endo*-2-*p*-chloro-4,6-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**11**) on the basis of the following data: ir (KBr) 6.20, 6.70, 9.18, 9.52, 12.20, 12.40, 13.52, 14.40, 14.60 μ; uv (95% ethanol) 247 nm (ε 22,700); nmr (60 MHz, $CDCl_3$) τ 7.60 (m, 1 H), 6.25 (t, 1 H, *J* = 2.5 and 2.0 Hz), 3.10 (broad s, 1 H), 2.75–1.85 (m, 14 H); *m/e* (parent) 344, 343, 267, 206, 103, and 102.

Anal. Calcd for $C_{21}H_{17}N_2Cl$: C, 76.63; H, 4.97; N, 8.12. Found: C, 76.48; H, 4.95; N, 8.09.

The filtrate was allowed to stand for several days at which time 0.68 g (40%) of *exo*-2-*p*-chlorophenyl-4,6-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**18**) precipitated: mp 138–139°; ir (KBr) 6.23, 6.75, 7.25, 8.55, 9.20, 9.50, 10.05, 11.35, 12.25, 12.35, 13.40, and 14.65 μ; uv (95% ethanol) 252 and 225 nm (ε 20,400 and 20,100); nmr (60 MHz) τ 7.40 (d, 1 H, *J* = 2.2 Hz), 6.40 (dd, *J* = 3.0 and 2.2 Hz, 1 H), 3.95 (d, 1 H, *J* = 2.2 Hz), 2.0–2.85 (*m*, 14 H); *m/e* 344 (M^+), 343, 342 (base), 341, 103, and 102.

Anal. Calcd for $C_{22}H_{17}N_2Cl$: C, 76.63; H, 4.97; N, 8.13. Found: C, 76.64; H, 5.00; N, 8.02.

Preparation of *trans*-2-*p*-Phenylbenzoyl-3-phenylaziridine. A solution containing 2.0 g of *trans*-4-phenylchalcone,[43] 1.8 g of iodine, 55 ml of methanol, and 75 ml of chloroform was saturated with ammonia. The solution was allowed to stir at room temperature for 2 hr. At the end of this time the solution had decolorized and was diluted with an equal volume of chloroform and washed with water. The chloroform layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure affording 1.9 g (88%) of *trans*-2-*p*-phenylbenzoyl-3-phenylaziridine: mp 122–126°; ir (KBr) 6.05, 6.25, 7.12, 7.95, 8.35, 9.70, 9.95, 11.60, 13.18, 13.65, 14.30, and 14.50 μ; uv (95% ethanol) 295 nm (ε 20,000); nmr (60 MHz, $CDCl_3$) τ 7.50 (m, 1 H), 6.90 (m, 1 H), 6.60 (m, 1 H), 2.0–3.0 (14 H, m); *m/e* (parent) 299, 297 (base), 284, 180, 179, 165, 153, 106, 105, 91, and 77.

***endo*- and *exo*-2,6-Diphenyl-4-(4′-phenyl)phenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene (15 and 19).** A suspension of 1.0 g of *trans*-2-*p*-phenylbenzoyl-3-phenylaziridine, 3 ml of benzaldehyde, and 0.1 g of ammonium bromide in 25 ml of absolute ethanol was saturated with ammonia at 0°. The solution was allowed to stand for 4 days at room temperature and the solvent was removed under reduced pressure. The crude solid was subjected to scanning liquid–liquid partition chromatography using a two-phase system prepared from 1000 ml of cyclohexene, 400 ml of dimethylformamide, 250 ml of ethyl acetate, and 30 ml of water.[44] The first peak in the chromatogram (0.28 g, 22%) was recrystallized from 95% ethanol to give pure *endo*-2,6-diphenyl-4-(4′-phenyl)phenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene (**15**): mp 170–171°; ir (KBr) 6.23, 6.82, 6.95, 7.15, 9.58, 9.98, 11.70, 12.95, 13.40, 13.70, 14.30, and 14.50 μ; uv (95% ethanol) 287 nm (ε 28,500); nmr (60 MHz, $CDCl_3$) τ 7.60 (m, 1 H), 6.25 (m, 1 H), 3.26 (m, 1 H), 1.92–3.0 (m, 19 H); *m/e* 386 (M^+), 384 (base), 179, 178, 105, 104, and 103.

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.88; H, 5.81; N, 7.18.

The second peak in the liquid–liquid partition chromatogram contained 0.93 g (73%) of a crystalline solid, mp 213–214°, whose structure is assigned as *exo*-2,6-diphenyl-4-(4′-phenyl)phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**19**) on the basis of the following data: ir (KBr) 6.30, 6.75, 6.95, 7.15, 7.98, 9.30, 9.52, 9.98, 10.40, 11.00, 11.40, 11.85, 13.05, 13.78, and 14.45 μ; uv (95% ethanol) 288 nm (ε 31,000); nmr (60 MHz, $CDCl_3$) τ 7.26 (*m*, 1 H), 6.22 (m, 1 H), 3.86 (m, 1 H), 1.90–2.94 (m, 19 H); *m/e* 386 (M^+), 385, 384, 383, and 178 (base).

(40) The thermal and photochemical cycloaddition of 1,3-diazabicyclo[3.1.0]hex-3-enes with a number of dipolarophiles has been investigated in some detail in our laboratory and will be reported on at a later date.

(41) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian 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 60 MHz with the Varian Associates high-resolution spectrometer and at 100 MHz using a Jeolco MH-100 spectrometer.

(42) N. H. Cromwell, R. D. Babson, and C. A. Harris, *J. Amer. Chem. Soc.*, **65**, 312 (1943).

(43) N. H. Cromwell, R. P. Cahoy, W. E. Franklyn, and G. D. Mercer, *ibid.*, **79**, 922 (1957).

(44) A. Padwa and L. Hamilton, *ibid.*, **89**, 102 (1967).

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.87; H, 5.68; N, 7.00.

Irradiation of *exo*- (or *endo*-) 2,4,6-Triphenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene in Benzene. A solution of 150 mg of diazabicyclohexene **5** (or 6) in 200 ml of benzene was irradiated with a 450-W Hanovia lamp using a Corex filter at 15° for 4 hr. The solvent was removed under reduced pressure at 15° giving a deep yellow oil (140 mg, 93%) whose structure is assigned as 1,3,6-triphenyl-2,5-diaza-1,3,5-hexatriene (**10**) on the basis of the following data. The infrared spectrum (film) was characterized by bands at 6.13, 6.32, 6.70, 6.90, 9.30, 9.72, 13.10, 13.40, 14.30, and 14.80 μ. The ultraviolet spectrum (95% ethanol) showed maxima at 240 and 360 nm (ϵ 19,000 and 12,000). The nmr spectrum (60 MHz, $CDCl_3$) showed a multiplet at τ 2.50 (16 H) and a singlet at τ 1.50 (2 H).

Chemical confirmation of the structure was obtained by the acid hydrolysis of **10**. A solution containing 300 mg of enediimine **10** and 3 ml of 10% hydrochloric acid in 25 ml of dioxane was stirred at room temperature for 3.5 hr. The mixture was diluted with water and made basic by adding 10% sodium bicarbonate. The aqueous solution was extracted with ether, dried over magnesium sulfate, and concentrated under reduced pressure to give 20 mg (9%) of 2,5-diphenylpyrazine, mp 192–193° (lit.[45] 194°). A mixture melting point with an authentic sample of 2,5-diphenylpyrazine was undepressed at 193–194°.

***cis*-2,3-Dihydro-2,3,5-triphenylpyrazine (8).** A solution containing 150 mg of enediimine **10** in 200 ml of benzene was heated at 50° for 1.5 hr in the dark. Removal of the solvent under reduced pressure gave 136 mg (91%) of a yellow solid which was recrystallized from 95% ethanol to give *cis*-2,3-dihydro-2,3,5-triphenylpyrazine (**8**) as yellow needles: mp 145–146°; ir (KBr) 6.40, 6.70, 6.90, 10.50, 13.10, 13.69, 14.35, and 14.55 μ; uv (95% ethanol) 276 nm (ϵ 7300); nmr (60 MHz, $CDCl_3$) τ 4.94 (m, 2 H), 1.98–2.89 (m, 15 H), 1.34 (d, 1 H, J = 1.5 Hz); *m/e* 310 (M^+), 309, 308, 307, 103, and 102 (base).

Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85; N, 9.03. Found: C, 84.90; H, 5.90; N, 8.90.

An authentic sample of **8** could also be prepared by the reaction of phenylglyoxal with *meso*-stilbenediamine.[46] A solution containing 0.27 g of phenylglyoxal and 0.42 g of *meso*-stilbenediamine in 25 ml of absolute ethanol was stirred at room temperature under a nitrogen blanket for 1 hr. The yellow solid which had precipitated from the reaction mixture was filtered and recrystallized from 95% ethanol to give a yellow solid, mp 145–146°. The infrared and nmr spectra of this material were identical with the product obtained from the thermolysis of enediimine **10**.

2,3,5-Triphenylpyrazine (9). Further chemical confirmation of **8** was obtained by the oxidation of *cis*-dihydropyrazine **8** to 2,3,5-triphenylpyrazine (**9**). A solution containing 0.31 g of *cis*-dihydropyrazine **8** and 50 mg of palladium on charcoal in 20 ml of benzene was heated at reflux for 12 hr. The catalyst was removed by filtration and the solvent was evaporated under reduced pressure to give 275 mg (89%) of 2,3,5-triphenylpyrazine (**9**): mp 152–153°; ir (KBr) 7.00, 7.27, 8.60, 9.05, 9.81, 12.82, 13.01, 13.20, 14.30, and 14.50 μ; uv (95% ethanol) 333, 295, 275, and shoulder at 235 nm (ϵ 16,400, 14,900, and 14,200); nmr (60 MHz, $CDCl_3$) τ 2.70–1.60 (15 H, m), 1.02 (1 H, s); *m/e* 308 (M^+), 307, and 102 (base).

Anal. Calcd for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.09. Found: C, 85.56, H, 5.32; N, 8.97.

An authentic sample of 2,3,5-triphenylpyrazine could also be prepared by reacting 2,5-diphenylpyrazine with phenyllithium. A suspension of 100 mg of 2,5-diphenylpyrazine and a 3-mol excess of phenyllithium in benzene was stirred at room temperature under nitrogen for 0.5 hr. The mixture was quenched with water and the resulting solution was extracted with ether. The ethereal layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure to give 62 mg (46%) of 2,3,5-triphenylpyrazine. This material was identical in all respects with that produced by the oxidation of *cis*- (or *trans*-) dihydropyrazine **8** (or **20**).

***trans*-2,3-Dihydro-2,3,5-triphenylpyrazine (20).** A solution of 0.27 g of phenylglyoxal and 0.42 g of *rac*-stilbenediamine[47] in 25 ml of absolute ethanol was allowed to stir for 1 hr at room temperature. Removal of the solvent under reduced pressure left a yellow oil which was crystallized from 95% ethanol to give 495 mg (80%) of *trans*-2,3-dihydro-2,3,5-triphenylpyrazine (**20**): mp 117–118°; ir (KBr) 6.25, 6.35, 6.67, 6.89, 7.92, 10.50, 10.60, 11.01, 12.91, 13.04, 14.20, and 14.50 μ; uv (95% ethanol) 266 nm (ϵ 7740); nmr (60 MHz, $CDCl_3$) τ 5.70 (broad s, 2 H), 1.83–3.10 (m, 15 H), and 1.53 (d, 1 H, J = 2.5 Hz); *m/e* 310 (M^+), 309, 308, 307, 103, and 102 (base).

Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85; N, 9.03. Found: C, 84.88; H, 5.89; N, 8.96.

Further confirmation of the structure of **20** was obtained by its oxidation to 2,3,5-triphenylpyrazine using palladium on charcoal in refluxing benzene.

Irradiation of *cis*- and *trans*-2,3-Dihydro-2,3,5-triphenylpyrazine in Benzene. A solution containing 100 mg of *cis*-**8** or *trans*-dihydropyrazine **20** in 250 ml of benzene was irradiated for 25 min using a 450-W Hanovia lamp equipped with a Pyrex filter at 15°. At the end of this time the original pale yellow solution turned deep yellow. The infrared and ultraviolet spectra of the oil that remained after removal of the solvent under reduced pressure at 15° were identical with that of 1,3,6-triphenyl-2,5-diaza-1,3,5-hexatriene (**10**). When a benzene solution of the enediimine was heated at 50° for 1.5 hr followed by removal of the solvent, a quantitative yield of *cis*-2,3,5-triphenyl-2,3-dihydropyrazine (**8**), mp 145–146°, was obtained.

Irradiation of *exo*- (or *endo*-) 2-*p*-Chlorophenyl-4,6-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene in Benzene. A solution containing 200 mg of *endo*- (or *exo*-) 2-*p*-chlorophenyldiazabicyclohexene (**11**) (or **18**) in 200 ml of benzene was irradiated at 15° for 30 min using a 450-W Hanovia lamp equipped with a Corex filter. Removal of the solvent *in vacuo* at 15° left a deep yellow oil whose structure is assigned as 1-*p*-chlorophenyl-3,6-diphenyl-2,5-diaza-1,3,5-hexatriene (**12**) on the basis of the following data: ir (film) 6.15, 6.25, 6.75, 9.20, 9.85, 12.00, 13.25, and 14.50 μ; uv (95% ethanol) 265 and 360 nm (ϵ 19,000 and 12,000); nmr (60 MHz, $CDCl_3$) τ 2.0–3.10 (m, 14 H), 1.80 (s, 1 H), and 1.60 (s, 1 H).

The photoproduct was taken up in benzene and heated at 50° for 2 hr. Removal of the solvent under reduced pressure gave an oil which was recrystallized from 95% ethanol to give 100 mg (50%) of *cis*-2,3-dihydro-2,5-diphenyl-3-*p*-chlorophenylpyrazine (**13**) as a yellow solid: mp 125–126°; ir (KBr) 6.40, 6.70, 9.15, 10.05, 12.20, 12.90, 13.45, 14.40, and 14.60 μ; uv (95% ethanol) 278 nm (ϵ 7750); nmr (60 MHz, $CDCl_3$) τ 4.88 (broad s, 2 H), 1.90–3.60 (m, 14 H), and 1.20 (broad s, 1 H); *m/e* 344 (M^+), 343, 342, 341, and 102 (base).

Anal. Calcd for $C_{22}H_{17}N_2Cl$: C, 76.63; H, 4.97; N, 8.12. Found: C, 76.33; H, 5.03; N, 8.01.

2,5-Diphenyl-3-*p*-chlorophenylpyrazine (14). Further confirmation of the structure of **13** was obtained by its oxidation to 2,5-diphenyl-3-*p*-chlorophenylpyrazine. A mixture of 261 mg of dihydropyrazine **13** and 172 mg of dichlorodicyanoquinone in 50 ml of benzene was refluxed for 1.5 hr. The solvent was removed under reduced pressure and the residue was filtered through a 6-in. column of Florisil using benzene as the eluent. Removal of the solvent afforded a white solid (52 mg, 20%) which was recrystallized from methanol to give pure 2,5-diphenyl-3-*p*-chlorophenylpyrazine (**14**): mp 146–147°; ir (KBr) 6.75, 7.05, 7.40, 8,.75, 9.25 9.95, 12.01, 12.40, 13.25, and 14.20 μ; uv (95% ethanol) 246, 296, and 334 nm (ϵ 18,300, 14,900, and 16,400); *m/e* 342 (M^+ and base), 341, and 102.

Anal. Calcd for $C_{22}H_{15}N_2Cl$: C, 77.06; H, 4.41; N, 8.18. Found: C, 76.99; H, 4.41; N, 7.96.

An authentic sample of **14** could also be prepared by the reaction of butyllithium and 1,4-bromochlorobenzene with 2,5-diphenylpyrazine. A solution containing 191 mg of 1,4-bromochlorobenzene and 96 mg of *n*-butyllithium was refluxed in 10 ml of ether for 0.2 hr. To this mixture was added a suspension of 232 mg of 2,5-diphenylpyrazine in 10 ml of benzene. The solution turned deep red and was allowed to stir at room temperature for 0.5 hr. The mixture was quenched with water and extracted with ether. The ethereal layer was dried over magnesium sulfate and the solvent was removed to give 300 mg (58%) of 2,5-diphenyl-3-*p*-chlorophenylpyrazine (**14**), mp 146–147°. The infrared spectrum of this material was identical with that of the material obtained from the oxidation of the dihydropyrazine.

Irradiation of 2,6-Diphenyl-4-(4′-phenyl)phenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene in Benzene. A solution containing 600 mg of *endo*- (or *exo*-) biphenylbicycloaziridine **15** (or **19**) in 450 ml of benzene was irradiated at 20° using a 450-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent at 20° under reduced pressure afforded an orange-yellow solid which was puri-

(45) F. Tutin, *J. Chem. Soc.*, 97, 2495 (1910).
(46) M. N. H. Irving and R. M. Parkins, *J. Inorg. Nucl. Chem.*, 27, 270 (1965).
(47) O. F. Williams and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, 81, 4466 (1959).

fied by washing with cold methanol, mp 140–144°. This material is assigned as 1,6-diphenyl-3-(4′-phenyl)phenyl-2,5-diaza-1,3,5-hexatriene (**16**) on the basis of the following data: ir (KBr) 6.15, 6.32, 6.71, 6.90, 7.10, 7.62, 9.90, 11.00, 12.95, 13.42, 13.80, 14.50 μ; uv (95% ethanol) 240, 280, and 365 nm (ε 18,400, 23,800, and 20,000).

cis-**2,3-Dihydro-2,3-diphenyl-5-(4′-phenyl)phenylpyrazine (17).** The above photoproduct was taken up in benzene and heated at 50° for 2 hr. Removal of the solvent gave 520 mg (98%) of **17**. Recrystallization from benzene–heptane gave an analytical sample: mp 168–169°; ir (KBr) 6.23, 6.35, 6.72, 6.90, 7.12, 9.35, 11.00, 12.95, 13.08, 14.70, and 14.45 μ; uv (95% ethanol) 247, 253, 257, 310 (ε 14,200, 14,500, 13,600, and 14,200); nmr (100 MHz, $CDCl_3$) τ 5.32 (m, 2 H), 2.22–3.60 (19 H, m), 1.92 (d, 1 H, J = 5.5 Hz); *m/e* 386 (M^+), 385, 384, 383, and 178 (base).

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.95; H, 5.66; N, 7.42.

An authentic sample of dihydropyrazine **17** could also be prepared by the reaction of *meso*-stilbenediamine with (4′-phenyl)-phenylglyoxal.[48] A solution containing 200 mg of *meso*-stilbenediamine and 204 mg of (4′-phenyl)phenylglyoxal in 50 ml of absolute ethanol was allowed to stir at room temperature for 0.5 hr. Removal of the solvent afforded a crude solid which was washed with ethanol and recrystallized from benzene–heptane, mp 168–169°. This material was identical with dihydropyrazine **17** prepared from the thermolysis of **16**.

trans-**2,3-Dihydro-2,3-diphenyl-5-(4′-phenyl)phenylpyrazine.** In a procedure identical with that used for the preparation of *cis*-dihydropyrazine **17**, *rac*-stilbenediamine was condensed with (4′-phenyl)phenylglyoxal. Recrystallization of the crude product from benzene–heptane gave *trans*-dihydropyrazine as a yellow solid: mp 199–200°; ir (KBr) 6.35, 6.75, 6.92, 7.14, 10.28, 10.72, 11.75, 13.75, and 14.35 μ; uv (95% ethanol) 247, 253, 257, and 308 nm (ε 14,200, 14,500, 14,200, and 14,200); nmr (100 MHz, $CDCl_3$) τ 6.10 (m, 2 H), 2.36–3.48 (m, 19 H), 1.98 (d, 1 H, J = 6.0 Hz); *m/e* 386 (M^+), 385, 384, 309, 179, and 178 (base).

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.90; H, 5.83; N, 6.99.

2,3-Diphenyl-5-(4′-phenyl)phenylpyrazine. A mixture of 293 mg of the *cis*-**17** or *trans*-dihydropyrazine and 172 mg of dichlorodicyanoquinone in 50 ml of benzene was heated at reflux for 1.5 hr. The solvent was removed and the residue was subjected to preparative thick layer chromatography to afford 87 mg (30%) of 2,3-diphenyl-5-(4′-phenyl)phenylpyrazine as a white crystalline solid: mp 182–183°, after recrystallization from benzene–heptane; ir (KBr) 7.08, 7.40, 7.62, 8.70, 9.12, 11.88, 13.10, 13.72, and 13.50 μ; uv (95% ethanol) 225, 305, and 343 nm (ε 21,700, 22,400, and 26,000); *m/e* 384 (M^+, base), 383, and 178.

Anal. Calcd for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.50; H, 5.16; N, 7.16.

Irradiation of *trans*-**2,3-Dihydro-2,3,5,6-tetraphenylpyrazine (21) in Benzene.** A solution containing 150 mg of *trans*-dihydropyrazine **21**, mp 195–197°,[49] in 200 ml of benzene was irradiated for 45 min using a 450-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent under reduced pressure gave 120 mg (80%) of *cis*-2,3-dihydro-2,3,5,6-tetraphenylpyrazine (**22**): mp 151–153°; ir (KBr) 6.45, 6.72, 6.95, 7.72, 10.10, 12.57, 13.00, 13.40, 13.65, 13.95, 14.25, and 14.75 μ; uv (95% ethanol) 260, 297, and 337 nm (ε 9000, 7680, and 4770); nmr (60 MHz, $CDCl_3$) τ 4.80 (s, 2 H), 2.40–3.25 (m, 20 H); *m/e* 386 (M^+), 384 (base), 383, and 178.

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.20; H, 5.76; N, 7.17.

Further confirmation of the structure of *cis*-dihydropyrazine **22** was obtained by its oxidation to tetraphenylpyrazine, mp 249–251° (lit.[50] 252–253°), using palladium on charcoal in refluxing benzene.

Irradiation of *trans*-**2,3-Dihydro-2,3,5,6-tetraphenylpyrazine (21) in Methanol.** A solution containing 1.0 g of *trans*-dihydropyrazine **21** in 1 l. of methanol was irradiated for 2 hr using a 450-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent under reduced pressure afforded a crude oil which was subjected to scanning liquid–liquid partition chromatography. The optical density trace revealed the presence of two products. The first peak amounted to 668 mg (62%) of a white solid, mp 170–172°, whose structure is assigned as 1-(methoxybenzyl)-2,3,5-triphenylimidazole (**29**) on the basis of the following data: ir (KBr) 6.23, 6.92, 7.30, 7.85, 9.10, 9.30, 9.70, 10.40, 10.85, 11.80, 13.45, and 14.40 μ; uv (methanol) 267 nm (ε 19,000); nmr (60 MHz, $CDCl_3$) τ 6.80 (s, 3 H), 3.87 (s, 1 H), 2.35–3.15 (m, 20 H); *m/e* 416, 297, 296 (base), 295, and 165.

The structure of imidazole **29** was established by hydrolysis to triphenylimidazole (**30**). A solution containing 100 mg of **29** in 10 ml of dioxane and 4 ml of a 5% hydrochloric acid solution was stirred for 2 hr at room temperature. The initial deep red color turned yellow as the reaction proceeded. The solution was diluted with water, made basic with 10% sodium bicarbonate solution, and extracted with ether. The ethereal layer was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure to give 72 mg of a crystalline solid, mp 271–272°. This material was identical in all respects with an authentic sample of triphenylimidazole (**30**).[51]

The second peak in the liquid–liquid partition chromatogram contained 130 mg (13%) of triphenylimidazole (**30**). No detectable quantities of *cis*-2,3-dihydro-2,3,5,6-tetraphenylpyrazine (**22**) were found in the chromatograph.

Irradiation of *cis*- **(or** *trans*-**) 2,3-Dihydro-2,3,5-triphenylpyrazine in Methanol.** A solution containing 310 mg of *cis*- (or *trans*-) dihydropyrazine **8** or **20** in 200 ml of methanol was irradiated for 1.5 hr using a 450-W Hanovia lamp fitted with a Pyrex filter. Evaporation of the solvent gave an oil which was subjected to liquid–liquid partition chromatography. The major product (185 mg, 60%) was a clear oil whose structure is assigned as 1-(methoxybenzyl)-2,4-diphenyl-3-imidazoline (**25**) on the basis of the following data: ir (film) 3.45, 6.15, 6.70, 6.90, 7.80, 8.55, 9.25, 9.72, 10.55, 13.30, 13.65, and 14.55 μ; uv (methanol) 245 and 280 nm (ε 10,500 and 1300); nmr (100 MHz, $CDCl_3$) τ 6.70 (s, 3 H), 6.15 (dd, 1 H, J = 14.0 and 5.5 Hz), 5.62 (dd, 1 H, J = 14.0 and 5.0 Hz), 5.07 (s, 1 H), 3.80 (t, 1 H, J = 5.0 Hz), and 2.60 (m, 15 H); *m/e* 308, 220, 145, 118, 106, 105, and 102.

Chemical confirmation was obtained by heating **25** with palladium on charcoal. A solution containing 200 mg of methoxyimidazoline **25** in 25 ml of benzene was heated at reflux for 48 hr with palladium on charcoal. Filtration of the catalyst and removal of the solvent gave 50 mg (25%) of 2,3,5-triphenylpyrazine (**9**).

Sodium Borohydride Reduction of 1-(Methoxybenzyl)-2,4-diphenyl-3-imidazoline. Structure **25** was further confirmed by reduction with sodium borohydride. A solution containing 300 mg of methoxyimidazoline **25** and a 10-mol excess of sodium borohydride was stirred in 25 ml of methanol at room temperature for 3.5 hr. The solution was diluted with 150 ml of ether and washed with water. The ethereal layer was dried over magnesium sulfate and the solvent was removed under reduced pressure to give 96 mg (35%) of a white solid which was recrystallized from ethanol, mp 89–90°. The structure of this material is assigned as 1-benzyl-2,4-diphenyl-3-imidazoline (**26**) on the basis of the following data: ir (KBr) 6.20, 6.70, 6.90, 7.35, 7.85, 8.55, 9.35, 11.85, 13.05, 13.40, and 14.55 μ; uv (methanol) 247 nm (ε 12,400); nmr (100 MHz, $CDCl_3$) τ 6.33 (AB quartet, 2 H, J = 13.0 Hz), 6.49 (dd, 1 H, J = 14.0 and 5.0 Hz), 5.82 (dd, 1 H, J = 14.0 and 4.5 Hz), 4.58 (t, 1 H, J = 4.5 Hz), 2.40–3.10 (m, 15 H); *m/e* 312, 219, 193, 118, and 91 (base).

Anal. Calcd for $C_{22}H_{20}N_2$: C, 84,58; H, 6.45; N, 8.97. Found: C, 84.20; H, 6.62; N, 9.39.

1-Benzyl-2,4-diphenylimidazole (27). The structure of imidazoline **26** was further established by oxidation to 1-benzyl-2,4-diphenylimidazole. A solution containing 175 mg of *N*-benzylimidazoline **26** in 25 ml of benzene was refluxed with excess palladium-on-charcoal catalyst for 12 hr. Filtration of the catalyst followed by removal of the solvent gave 71 mg (40%) of 1-benzyl-2,4-diphenylimidazole (**27**) as a white solid: mp 124–125°; ir (KBr) 6.28, 6.84, 6.96, 7.20, 7.48, 8.52, 9.38, 9.85, 10.60, 10.92, 12.95, and 14.50 μ; uv (methanol) 266 nm (ε 21,400); nmr (100 MHz, $CDCl_3$) τ 4.90 (s, 2 H), 2.10–3.10 (m, 16 H); *m/e* 310 (M^+), 219, 116, 91 (base), and 89.

Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85; N, 9.03. Found: C, 85.00; H, 5.90; N, 8.90.

1-Benzyl-2,4-diphenylimidazole could also be prepared by reacting 2,4-diphenylimidazole with benzyl bromide. A mixture of 265 mg of 2,4-diphenylimidazole, 206 mg of benzyl bromide, and an excess of sodium hydride in 25 ml of xylene was refluxed for 6 hr. The reaction was quenched with ethanol and filtered to re-

(48) L. Mauri and D. Nardi, *Farmaco, Ed. Prat.*, **18** (12), 651 (1963).
(49) T. Hayashi, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, **39**, 89 (1941).
(50) A. Rosenthal, *Can. J. Chem.*, **38**, 2025 (1960).
(51) G. E. Philbrook, M. A. Maxwell, R. E. Taylor, and J. R. Trotter, *Photochem. Photobiol.*, 4, 1175 (1965).

move the inorganic residues. The solvent was removed under reduced pressure to give a crystalline solid. Recrystallization from 95% ethanol gave white needles, mp 124–125°. This material was identical in all respects with a sample of the solid obtained from the oxidation of *N*-benzyl-2,4-diphenylimidazoline.

Irradiation of *exo*- (or *endo*-) 2,4,6-Triphenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene in Methanol. A solution containing 350 mg of the bicycloaziridine in 400 ml of methanol was irradiated for 3 hr using a 450-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent under reduced pressure left a yellow oil which was subjected to scanning liquid–liquid partition chromatography. The major component of the mixture (140 mg, 40%) was identified as 1-(methoxybenzyl)-2,4-diphenyl-3-imidazoline (**25**). The same imidazoline could be prepared by treating 1,3,6-triphenyl-2,5-diaza-1,3,5-hexatriene (**10**) with methanol in the dark.

Irradiation of *endo*-2,4-Diphenyl-6-*p*-nitrophenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene (31) in Methanol. A solution containing 900 mg of *endo*-2,4-diphenyl-6-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**31**), mp 173–174° (lit.[23] 174–175°), in 450 ml of methanol was irradiated for 3.5 hr using a 450-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent left an oil which was purified by liquid–liquid partition chromatography. The major fraction (380 mg, 42%) was recrystallized from 95% ethanol to give 1-*p*-nitrobenzyl-2,4-diphenylimidazole (**32**) as white needles: mp 116–117°; ir (KBr) 6.62, 7.15, 7.45, 8.45, 10.58, 11.92, 12.30, 12.95, 13.62, and 14.35 μ; uv (95% ethanol) 268 nm (ϵ 30,800); nmr (100 MHz, $CDCl_3$) τ 4.82 (s, 2 H), 1.90–3.80 (m, 15 H); *m/e* 220, 95, 81, 71, and 69 (base).

Anal. Calcd for $C_{22}H_{17}N_3O_2$: C, 74.35; H, 4.82; N, 11.84. Found: C, 74.51; H, 5.00; N, 11.78.

An authentic sample of **32** could be prepared by treating 2,4-diphenylimidazole with *p*-nitrobenzyl bromide. A solution containing 150 mg of 2,4-diphenylimidazole and 150 mg of *p*-nitrobenzyl bromide in 25 ml of xylene was heated at reflux for 15 hr. Removal of the solvent under reduced pressure left a crude red oil which was subjected to preparative thick-layer chromatography. The major component of the mixture amounted to 44 mg (20%) of 1-*p*-nitrobenzyl-2,4-diphenylimidazole (**32**), mp 116–117°. This material was identical in all respects with that produced from the irradiation of **31**.

Irradiation of *endo*- and *exo*-2,4,6-Triphenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene with Dimethyl Acetylenedicarboxylate. A solution containing 300 mg of diazabicyclohexene **5** (or **6**) and 140 mg of dimethyl acetylenedicarboxylate in 60 ml of benzene was irradiated with a 450-W Hanovia mercury lamp for 2.5 hr. Removal of the solvent at 50° under reduced pressure gave a dark oil whose nmr spectrum indicated the complete absence of 2,3-dihydro-2,3,5-triphenylpyrazine. Recrystallization of the oil from 95% ethanol gave a 72% yield of dimethyl (3*R**,7*R**,7a*S**)-7,7a-dihydro-1,3,5-triphenyl-3*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (**34**) as a white crystalline solid: mp 123–124°; ir (KBr) 5.80, 6.15, 6.95, 7.95, 10.60, 12.30, 13.40, 14.10, and 14.40 μ; uv (95% ethanol) 240 nm (ϵ 19,000); nmr (100 MHz, pyridine-d_5) τ 6.62 (3 H, s), 6.58 (3 H, s), 4.54 (d, 1 H, J = 4.0 Hz), 3.80 (d, 1 H, J = 4.0 Hz), 3.62 (t, 1 H, J = 4.0 Hz), 1.96–3.02 (m, 15 H); *m/e* 452 (M^+), 450, 391, 285, 105, and 104 (base).

Anal. Calcd for $C_{28}H_{24}O_4N_2$: C, 74.32; H, 5.35; N, 6.19. Found: C, 73.94; H, 5.12; N, 6.15.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant GP-24449) and the National Institutes of Health (Grant No. CA-12195-06).

Photochemistry of Cyclopentenones. Hydrogen Abstraction by the β-Carbon Atom

Steven Wolff, William L. Schreiber, Amos B. Smith, III, and William C. Agosta*

Contribution from the Laboratories of The Rockefeller University, New York, New York 10021. *Received April 26, 1972*

Abstract: Photochemical isomerization reactions are described for three cyclopentenones, **7**, **19**, and **24**. Irradiation of **7** leads to **8**, **9**, and **10**; **19** gives **21**; and **24** leads to **26**, **27**, and **28**. These products are most readily derived from intermediate biradicals **16**, **20**, and **25**, formed by intramolecular abstraction of a side-chain hydrogen atom by the β-carbon atom of the enone system. Direct proof of this hydrogen transfer was obtained using deuterium-labeled **7** (**17**). Structures of bicyclic products **10** and **21** were proved by photochemical degradation to **15** and **23**, respectively, which were independently synthesized. Treatment of acyloin **36** with polyphosphoric acid provided an independent synthesis of **10** through a 1,5-hydride transfer reaction. Preparation of starting cyclopentenones and related compounds is described.

In an earlier investigation[1] into the photochemical reactions of simple cyclopentenones, we observed that irradiation of 4,4-dimethylcyclopentenone (**1**) in *tert*-butyl alcohol led to 2-*tert*-butoxy-4,4-dimethylcyclopentanone (**2**). That is, in a cyclopentenone in which type I (α cleavage)[2] and type II (γ abstraction)[2,3] processes were disfavored by lack of substitution at C(5), α addition of solvent was a significant photochemical reaction. This is in contrast to previous reports[4–6] of light-induced addition of hydroxylic solvent to several unsaturated ketones, including 5,5-dimethylcyclohexenone (**3**),[6] a simple homolog of ketone **1**. In all these latter cases, the solvent addition is β, leading for example to **4**[6] from **3**, and apparently the reaction involves ionic addition of solvent to a photoexcited ketone or some species derived from it.[4] Apart from these formal Michael reactions, however, both

(1) W. C. Agosta and A. B. Smith, III, *J. Amer. Chem. Soc.*, **93**, 5513 (1971).

(2) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, Chapter 5.

(3) P. J. Wagner, *Accounts Chem. Res.*, 4, 168 (1971), and references cited therein.

(4) B. J. Ramey and P. D. Gardner, *J. Amer. Chem. Soc.*, **89**, 3949 (1967); P. de Mayo and J. S. Wasson, *Chem. Commun.*, 970 (1967).

(5) G. Bozzato, K. Schaffner, and O. Jeger, *Chimia*, **20**, 114 (1966); O. L. Chapman, J. B. Sieja, and W. L. Welstead, Jr., *J. Amer. Chem. Soc.*, **88**, 161 (1966); T. Matsuura and K. Ogura, *Bull. Chem. Soc. Jap.*, **40**, 945 (1967).

(6) W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968).