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Photogeneration and Reactivity of 1,*n*-Diphenyl-1,*n*-azabiradicals

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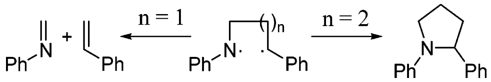
Received January 30, 2006

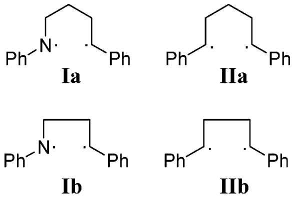


The 1,5-diphenyl-1,5-azapentanediyl biradical **Ia** was generated by photolysis of 1,2-diphenylazacyclopentane (pyrrolidine **1a**). Among the reaction pathways followed by **Ia**, C−N bond reformation with ring closure was found to be the predominating process, as determined by separate irradiation of either of the pure enantiomers of **1a**. Disproportionation was a minor process and took place only via H abstraction by the C5 benzylic radical. Another minor pathway was C5-aryl coupling, with formation of 5-phenyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (**4a**), which is equivalent to photo-Claisen rearrangement of **1a**. Likewise, the 1,4-diphenyl-1,4-azabutanediyl biradical **Ib** was generated by photolysis of 1,2-diphenylazacyclobutane (azetidine **1b**). This species underwent predominating C2−C3 cleavage, as indicated by the extensive styrene formation. Although N1−C4 bond reformation also took place, this is not the major pathway occurring from **Ib**. Besides, C4-aryl coupling to give 4-phenyl-1,2,3,4-tetrahydroquinoline (**4b**) was also observed. All the possible reaction pathways were theoretically studied at the UB3LYP/6-31G* computational level; the results were found to be in good agreement with the experimental observations.

Introduction

Biradical intermediates play an important role in many thermal and photochemical processes. 1,*n*-Diaryl-1,*n*-alkanediyl biradicals (as for example, **IIa** and **IIb** in Chart 1) have been proposed as intermediates in a wide range of reactions such as the geometric photoisomerization of cycloalkanes,[1] the dimerization of styrenes,[2] and the photoextrusion of CO_2, N_2, SO_2, or CO in lactones,[3] cyclic azoalkanes,[4] sulfones,[5] or ketones,[6,7a,b] respectively. They have also been generated via two-photon two-laser photolysis of 1,*n*-dichloro-1,*n*-diphenylalkanes.[7,8]

CHART 1. Structures of 1,*n*-Azabiradicals Ia and Ib and Their All-Carbon Analogues IIa and IIb



Comparatively little is known about the analogous aza biradicals (**Ia** and **Ib** in Chart 1). A related precedent was published by Platz and Burns.[9] They were able to generate the 1-imino-8-naphthoquinomethane biradical (together with 1-methyl-8-nitrenonaphthalene) upon photolysis of 1-azido-8-methyl-

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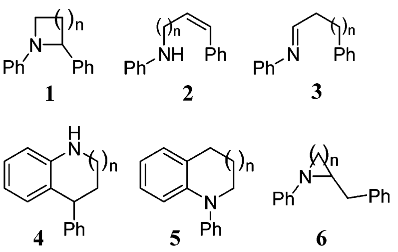
CHART 2. Structural Formulas of Compounds 1−6



a, n = 2
b, n = 1

naphthalene in a 2-methyltetrahydrofuran matrix at 77 K; the structure was assigned by means of ESR. Nitrogen-centered biradicals have also been proposed as intermediates in the photochemistry of pyrrolidones and bichromophoric styrene−amine systems.[10] However, a systematic study on the formation and behavior of this type of biradical has not yet been carried out.

We became interested in the chemistry of 1,5-diphenyl-1,5-azapentanediyl biradical (**Ia**) as a logical extension of our previous studies on the C-centered analogue **IIa**, which is known to undergo cyclization to 1,2-diphenylcyclopentanes or disproportionation to 1,5-diphenylpentenes.[7a,c]

Likewise, the 1,4-diphenyl-1,4-azabutanediyl biradical **Ib** is the aza analogue of **IIb**, which produces a mixture of 1,2-diphenylcyclobutane, styrene, and 1-phenyl-1,2,3,4,-tetrahydronaphthalene as a result of cyclization, cleavage, and ortho coupling processes, respectively.[7b]

In this context, we report here on the unambiguous generation of 1,*n*-azabiradicals by photolysis of the 1,2-diphenylazacycloalkanes, as well as on their fate, as revealed by the analysis of the final products. Theoretical calculations on the possible reaction pathways have also been performed to rationalize the experimental data.

Results and Discussion

1,5-Azabiradical. Biradical **Ia** was generated by 254 nm photolysis of pyrrolidine **1a** (Chart 2), which was obtained following a literature procedure.[10b] After homolytic C−N bond cleavage, the possible pathways available for **Ia** are (i) C−N bond reformation with ring closure leading back to the starting material, (ii or iii) disproportionation, and (iv or v) C−C or C−N coupling with intramolecular rearrangement (see Scheme 1). Chemical evidence for the pathways actually occurring from **Ia** was obtained by analysis of the final product distribution.

As stated above, C−N bond reformation along route (i) would lead back to pyrrolidine **1a**. In this context, it is worth mentioning that even after prolonged irradiation most of the starting **1a** remained apparently "unreacted". To determine whether (and if so, to what extent) retrocyclization was actually occurring, racemic **1a** was resolved into the two pure enantiomers by means of HPLC equipped with a semipreparative chiral column. Then parallel irradiation of the two enantiomers was conducted until the degree of conversion into other products was about 5%. Analysis of the pyrrolidine fraction by chiral HPLC revealed that the extent of inversion from either of the two **1a** enantiomers was about 10% (Figure 1). If one assumes that pathway (i) occurs without any significant enantioselectivity under the employed reaction conditions, 10% inversion of the configuration would be equivalent to 20% reformation of **1a** after C−N bond homolysis. In other words, route (i) would represent about 80% of all the processes actually occurring from **Ia**.

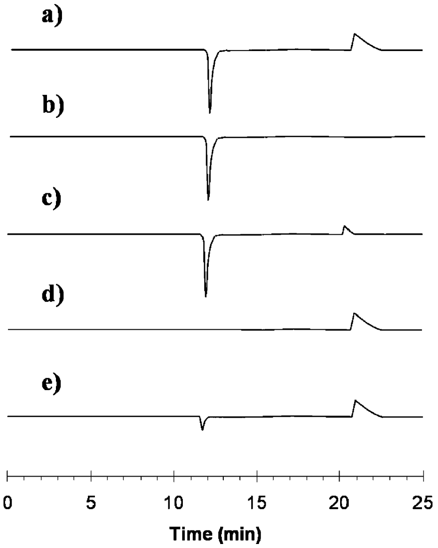
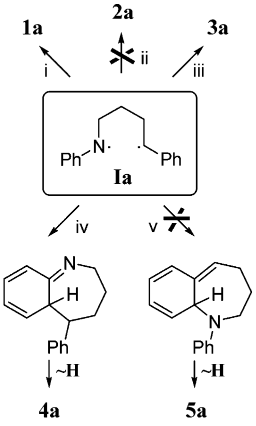


FIGURE 1. Chiral HPLC analysis of (a) racemic **1a**, (b) and (d) its two pure enantiomers, and (c) and (e) separate irradiation of each enantiomer.

SCHEME 1. Mechanistic Pathways Available for the 1,5-Azabiradical Ia



In any case, retrocyclization must be by far the major reaction pathway; thus, even if it ensues with complete inversion of configuration, it would still represent two-thirds (10% vs 10 + 5%) of all the processes occurring from **Ia**. However, if there is some "memory of chirality" during ring closure, more than 80% of biradical **Ia** would be following this pathway. In this context, the multiplicity of the biradical (singlet vs triplet) would play an important role. Although no experimental evidence was obtained by means of transient absorption measurements, calculations showed that the two states are nearly degenerate (see below). This suggests that the most feasible situation is retrocyclization with a high degree of racemization.

In regard to the two possible disproportionation processes, no evidence was obtained for route (ii), because not even traces of alkene **2a** were detected. Conversely, route (iii) seems to

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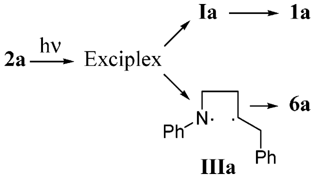
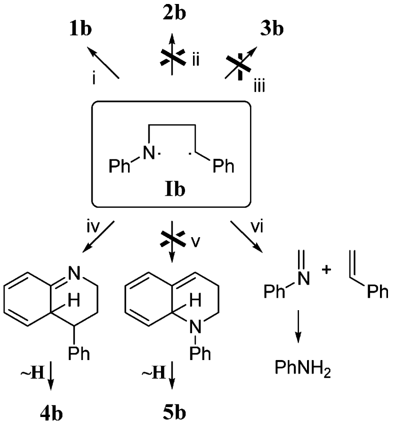
SCHEME 2. Mechanism Proposed by Lewis Explaining Photoproducts Formation by Irradiation of 2a



SCHEME 3. Mechanistic Pathways Available for the 1,4-Azabiradical Ib



play some role, as indicated by the formation of 4-phenylbutanal and aniline, the obvious hydrolysis products of imine **3a**.

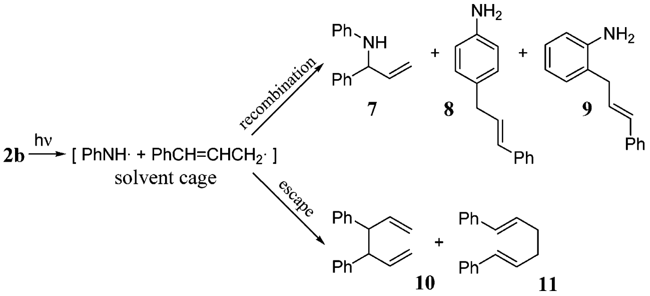
Finally, of the two possible products of intramolecular rearrangement, only **4a** was obtained. Its formation occurs through route (iv), which involves the typical Claisen rearrangement with 1,3-benzyl migration.[11] The alternative rearrangement product with C−N coupling (**5a**) was not formed.

In a previous work, Lewis studied the photochemistry of *N*-(4-phenylbut-3-enyl)aniline **2a**.[10b] After irradiation, this bichromophoric aniline/styrene system was found to undergo an intramolecular photocyclization process (Scheme 2), with formation of **1a** as major photoproduct. Besides, GC-MS analysis revealed the formation of 2-benzyl-1-phenylazetidine (**6a**) and several other unidentified minor products. As this constitutes an alternative generation of the 1,5-diphenyl-1,5-azabiradical **Ia**, all the compounds obtained by irradiation of **2a** and indicated in Scheme 1 should also be found in the photolysis mixture from **1a**. As a matter of fact, when we irradiated *N*-(4-phenylbut-3-enyl)aniline (**2a**) under the same conditions as **1a**, minor amounts of compound **4a** were actually obtained.

1,4-Azabiradical. Biradical **Ib** was generated by the irradiation of azetidine **1b** (Chart 2), which was also synthesized following a known method.[12] As in the case of **Ia**, several pathways are available for **Ib** after homolytic C−N bond cleavage: (i) C−N bond reformation with ring closure leading back to the starting material, (ii or iii) disproportionation, (iv or v) C−C or C−N coupling with intramolecular rearrangement, and (vi) C2−C3 cleavage to afford olefin and imine units (see Scheme 3).

The first pathway, C−N bond reformation along route (i), would lead back to azetidine **1b**. In this context, it has to be stressed that compound **1b** reacted about 10 times faster than its higher homologue **1a** under the same irradiation conditions. As for **1a**, the extent of retrocyclization was determined in this case by parallel irradiation of the two enantiomers of **1b**. After 20% conversion, analysis of the azetidine fraction by chiral HPLC showed that the degree of configuration inversion from either of the two **1b** enantiomers was about 5%. Taking into account the above discussion, route (i) would represent about one-third of all the processes actually occurring from **Ib**.

SCHEME 4. Main Photoproducts Resulting from Irradiation of 2b



Disproportionation to compounds **2b** or **3b** was not detected in the reaction mixture. Likewise, not even traces of **5b** were observed. However, a small amount of the Claisen rearrangement product **4b** was indeed found in the photolyzate. By far, the predominating process for the 1,4-azabiradical **Ib** was cleavage of the C2−C3 bond, as indicated by the extensive formation of styrene (process vi in Scheme 3).

Although the photochemistry of *N*-cinnamylaniline **2b** (Chart 2) has not been the subject of previous studies, we wondered whether its behavior could be analogous to that of its higher homologue **2a**. If so, photolysis of **2b** should occur via H transfer in an intramolecular exciplex, leading to the 1,4-azabiradical **Ib** and providing an alternative entry to this intermediate. However, in this case, the only observed process was C−N cleavage to afford a radical pair and all the coupling products (in-cage and out-of-cage) derived therefrom. This is summarized in Scheme 4.

Theoretical Studies. The possible reaction channels were theoretically studied at the UB3LYP/6-31G* computational level. For the 1,5-azabiradical **Ia**, five reaction channels were considered (see Scheme 1) involving five transition states, **TS1a**−**TS5a**, two intermediates, **IN4a** and **IN5a**, and three products, **1a**−**3a**, which were located and characterized. The total and relative energies are summarized in Table 1, while the geometries of the transition structures (TSs) are given in Figure 2.

The most favorable reactive channel corresponds to cyclization, to give pyrrolidine **1a** via **TS1a**. The process is almost barrierless and strongly exothermic (−50.9 kcal/mol). For the disproportionation reactions, hydrogen abstraction by the C5-centered radical via **TS3a** is 3.3 kcal/mol more favorable than by the N1-centered radical via **TS2a**. Both reactions are also very exothermic processes, −46.7 and −41.8 kcal/mol. Finally, for intramolecular radical attack to the two aromatic rings, the energy of **TS4a** is 5.5 kcal/mol lower than that of **TS5a**. In addition, formation of **IN4a** is also 7.0 kcal/mol more exothermic than that of **IN5a**. These results indicate that the most favorable reaction channels are those proceeding through **TS1a**, **TS3a**, and **TS4a**, in clear agreement with the experimental findings. Thus, processes involving attack by the C-centered radical (channels iii and iv) are clearly favored over those

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TABLE 1. UB3LYP/6-31G* Total (in au) and Relative (in kcal/mol) Energies of the Stationary Points Involved in the Reactions of the 1,5- and 1,4-Azabiradicals Ia and Ib

	E	ΔE
Ia	−674.612 038	
TS1a	−674.609 753	1.4
TS2a	−674.591 593	12.8
TS3a	−674.596 918	9.5
TS4a	−674.601 312	6.7
TS5a	−674.592 697	12.1
1a	−674.693 157	−50.9
2a	−674.678 661	−41.8
3a	−674.686 381	−46.7
IN4a	−674.644 664	−20.5
IN5a	−674.633 548	−13.5
Ib	−635.299 171	
TS1b	−635.288 351	6.8
TS2b	−635.264 134	23.7
TS3b	−635.267 275	20.0
TS4b	−635.297 475	1.1
TS6b	−635.294 029	3.2
1b	−635.355 189	−35.2
2b	−635.362 715	−39.9
3b	−635.370 033	−44.5
IN4b	−635.342 536	−27.2
imine[a] + styrene	−635.334 448	−22.1

[a] The imine of aniline with formaldehyde.

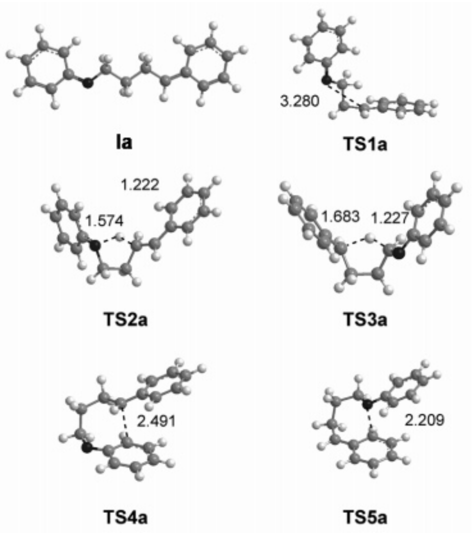

FIGURE 2. Geometries of the 1,5-azabiradical **Ia** and the transition structures **TS1a−TS5a** involved in the reactions of **Ia**. Bond lengths between the atoms directly involved in the reaction are given in angstroms.

associated with the less-reactive N-centered radical (channels ii and v). This is schematically shown in Figure 3.

In regard to the geometries of the TSs involved in the reactions of **Ia** given in Figure 2, analysis of the atomic movement at the unique imaginary frequency of **TS1a** (28.9i cm^{-1}) indicates that this TS is mainly associated with the C2−C3 bond rotation. Intramolecular biradical coupling with formation of the N1−C5 bond is nearly barrierless. For the TSs corresponding to the disproportionation reactions, the lengths of the forming and breaking bonds are: 1.574 Å (N1−H) and 1.222 Å (C4−H) at **TS2a** or 1.683 Å (C5−H) and 1.227 Å (C2−H) at **TS3a**. Finally, at the TSs corresponding to intramolecular radical attack to the aromatic rings, the lengths of the forming bonds are 2.491 Å (C5−C(Ar)) at **TS4a** and 2.209 Å (N1−C(Ar)) at **TS5a**.

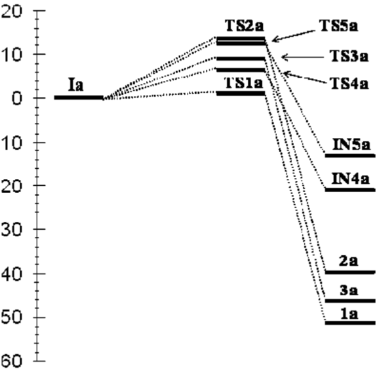

FIGURE 3. Energy profile (in kcal/mol) for all the possible reaction channels of **Ia**.

The extent of bond formation along a reaction pathway is provided by the concept of bond order (BO).[13] The BO value of the N1−C5 forming bond at **TS1a** is 0.01, a very low value indicating that bond formation is not yet initiated. Note that this TS has been associated with the C2−C3 bond rotation. At the TSs corresponding to the disproportionation reactions, the BO values of the forming and breaking bonds are 0.23 (N1−H) and 0.60 (C4−H) at **TS2a**, as compared with 0.23 (C5−H) and 0.64 (C2−H) at **TS3a**. These values point to asynchronous bond-forming and bond-breaking processes, where the latter are slightly more advanced than the former. Finally, at the TSs associated with radical attack to the aromatic rings, the BO values of the forming bonds are 0.21 (C5−C(Ar)) at **TS4a** and 0.32 (N1−C(Ar)) at **TS5a**. Bond formation at the more favorable **TS4a** is more delayed than at **TS5a**.

The initial $\langle S^2 \rangle$ values for the singlet biradical **Ia** (1.04) became 0.49 after spin annihilation. These deviations of $\langle S^2 \rangle$ from zero indicate that the biradical species are not pure singlet spin states.[14] A value of the unity for $\langle S^2 \rangle$ indicates a 1:1 mixture of singlet and triplet states.[15] Analysis of the total atomic spin density in biradical **Ia** indicated that it is mainly located at the nitrogen atom (−0.63) and at the benzylic carbon (0.76). At the UB3LYP/6-31G* level, the triplet biradical **Ia**, with $\langle S^2 \rangle = 2.06$, lies only 0.1 kcal/mol above the singlet biradical. However, the atomic spin density at the nitrogen atom now has a positive value (0.63), indicating that both electrons have α spin. Otherwise, both degenerated singlet and triplet biradicals have identical geometrical and electronic structures.

For the 1,4-azabiradical **Ib**, five reaction channels were also considered (see Scheme 3) involving five transition states (**TS1b−TS4b** and **TS6b**), one intermediate (**IN4b**), and five products (**1b−3b**, styrene, and the imine of aniline with formaldehyde), which were located and characterized. The total and relative energies are summarized in Table 1, while the geometries of the TSs are given in Figure 4.

According to DFT calculations, coupling of the C4-centered radical of **Ib** with the aromatic carbon ortho to the nitrogen atom (ultimately leading to **4b** after 1,3-H migration) is a

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(13) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083−1096.

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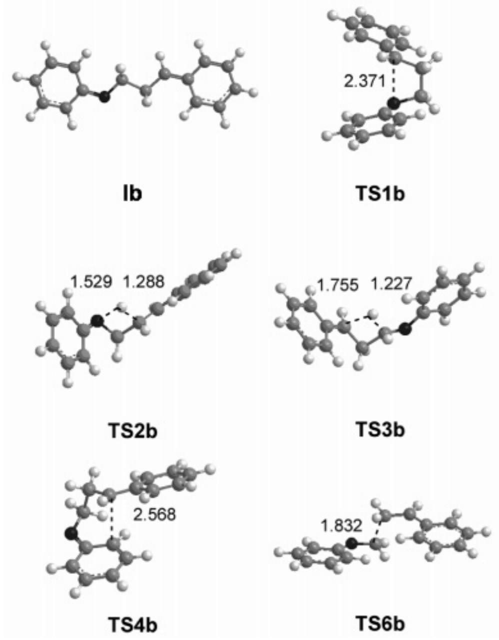

FIGURE 4. Geometries of the 1,4-azabiradical **Ib** and the transition structures **TS1b**−**TS4b** and **TS6b** involved in its reactions. Bond lengths between the atoms directly involved in the reaction are given in angstroms.

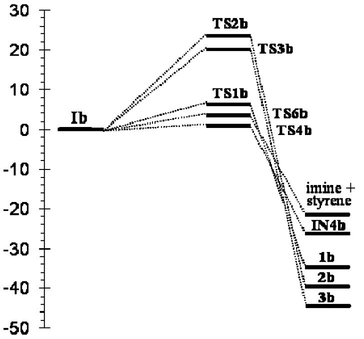

FIGURE 5. Energy profile (in kcal/mol) for all the possible reaction channels of **Ib**.

feasible reactive channel. At this computational level, the process (channel iv) appears to be barrierless. The favorable boat arrangement of the six-membered **TS4b** accounts for its low activation energy. On the other hand, C2−C3 bond cleavage via **TS6b** (channel vi) also presents a very low barrier, 3.2 kcal/mol. The ring-closure process via **TS1b** (channel i), with the formation of azetidine **1b**, presents an activation energy of 6.8 kcal/mol, somewhat higher than that calculated for the formation of pyrrolidine **1a**; the higher strain associated with closure of a four-membered ring accounts for this difference. By contrast, the disproportionation reactions ii and iii present large activation energies. The four-membered cyclic arrangements required for this intramolecular hydrogen abstraction reaction account for the large energy of **TS2b** and **TS3b**. This is schematically shown in Figure 5.

All the possible reactions shown in Scheme 3 are exothermic (between −22 and −45 kcal/mol). Again, formation of the four-membered azetidine **1b** is 15.7 kcal/mol less exothermic than formation of five-membered pyrrolidine **1a**, in clear agreement with the larger ring strain associated with the four-membered ring.

The geometries of the TSs involved in the reactions of 1,4-azabiradical **Ib** are given in Figure 4. In **TS1b**, the N1−C4 distance is 2.371 Å and the N1−C2−C3−C4 dihedral angle is only −24.8 degrees, pointing to a nearly planar arrangement. Analysis of the atomic movement at the unique imaginary frequency of **TS1b** (265.5i cm^{-1}) indicates that this TS is mainly associated with N1−C4 bond formation. For the TSs corresponding to the disproportionation reactions, the lengths of the forming and breaking bonds are 1.529 Å (N1−H) and 1.288 Å (C3−H) at **TS2b** or 1.755 Å (C4−H) and 1.227 Å (C2−H) at **TS3b**. In **TS4b**, associated with C4 radical attack to the aromatic ring, the length of the C4−C(Ar) forming bond is 2.568 Å; this value is larger than that found for C−C bond formation at **TS4a**.

In regard to the BOs, the N1−C4 BO value at **TS1b** is 0.21; this points to an early bond formation.[16] At the TSs associated with the disproportionation reactions, the BO values of the forming and breaking bonds are 0.27 (N1−H) and 0.53 (C3−H) at **TS2b** or 0.15 (C4−H) and 0.70 Å (C2−H) at **TS3b**. At **TS4b**, corresponding to C4 radical attack to the aromatic ring, the BO value of the C−C forming bond is 0.13 (C4−C(Ar)). Thus, bond formation at **TS4b** is less advanced than at **TS4a**. Finally, at **TS6b**, the C2−C3 BO value is 0.63; hence, bond cleavage has already started.

The initial $\langle S^2 \rangle$ values for the singlet biradical **Ib** (1.04) became 0.49 after spin annihilation. Analysis of the total atomic spin density in biradical **Ib** indicated that it is mainly located at the nitrogen atom (−0.63) and at the benzylic carbon (0.76). At the UB3LYP/6-31G* level, the triplet biradical **Ib**, with $\langle S^2 \rangle = 2.06$, lies 0.5 kcal/mol above the singlet biradical. However, the atomic spin density at the nitrogen atom has a positive value (0.64), indicating that both electrons have a α spin. Otherwise, both species have identical geometrical and electronic structures.

For biradicals **Ia** and **Ib**, both singlet and triplet states are degenerated. However, as a result of the fact that products and intermediates of Scheme 3 have closed-shell configurations, the reaction paths associated with the triplet state are very disfavored due to the formation of triplet excited species.[16,17]

Conclusion

The chemistry of 1,5-diphenyl-1-azapentanediyl biradical **Ia** is dominated by intramolecular N−C coupling, to give the five-membered ring product (i.e., pyrrolidine **1a**). Disproportionation is a minor process and takes place only in one sense: abstraction of the H atom α to the N center by the C5 benzylic radical. Another minor pathway is C5−C(Ar) coupling, with formation of **4a** (equivalent to the photo-Claisen rearrangement of **1a**). This behavior is analogous to that of the 1,5-diphenyl-1,5-pentanediyl biradical, although in the all-carbon case, the extent of disproportionation is much higher,[6a,7a] and no C5-aryl coupling with formation of a seven-membered ring is observed. In regard to the 1,4-derivatives, the behavior of the 1,4-diphenyl-1,4-butanediyl biradical is very similar to that of its 1-aza analogue; the predominating process is C2−C3 cleavage (detected through the formation of styrene), although C1−C4 (or N1−C4) coupling to give the four-membered rings also takes place to a significant extent. C4-aryl coupling is in both cases a minor process. A good correlation is observed between the

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experimental results and the theoretical calculations at the UB3LYP/6-31G* computational level.

Experimental Section

Chemicals. Compounds **1a**,[10b] **1b**,[12] **2a**,[10b] and **2b**[18] (see structures in Chart 1) were prepared following the literature methods. Isolation and purification were done by conventional column chromatography on silica gel, using hexane/dichloromethane as eluent. Isolation of the pure enantiomers of **1a** and **1b** was performed by semipreparative HPLC equipped with a chiral column, employing 2-propanol/hexane as eluent.

Photoproducts **4a**,[19] **4b**,[20] **7**,[21] **8**,[18] **9**,[18] **10**,[22] and **11**[22] were known and their structures were confirmed by comparison of their spectroscopic data with those reported in the literature. Aniline, 4-phenylbutanal, and styrene were identified by comparison with authentic samples.

General Irradiation Procedure. Solutions of 1 mg/mL of the substrate in HPLC grade acetonitrile were irradiated at room temperature through quartz, with a multilamp photoreactor equipped with eight lamps emitting at 254 nm (monochromatic). The photoreaction course was followed by means of GC/MS and ^{1}H NMR.

The photoproducts obtained upon irradiation of the different substrates are given below; the product distributions are indicated in parentheses.

Irradiation of **1a** (4 h, 24% conversion): 4-phenylbutanal + aniline (57%) and **4a** (43%).

Irradiation of **1b** (30 min, 30% conversion): styrene (93%) and **4b** (7%).

Irradiation of **2b** (2h, 55% conversion): **7** (25%), **8** (11%), **9** (6%), **10** (33%), and **11** (25%).

Computational Methods. DFT calculations were carried out using the B3LYP[23] exchange-correlation functionals, together with the standard 6-31G* basis set.[24] For all DFT calculations, the unrestricted formalism (UB3LYP) was employed. Optimizations were carried out using the Berny analytical gradient optimization method.[25] The stationary points were characterized by frequency calculations to verify that the TSs have one and only one imaginary frequency. The intrinsic reaction coordinate[26] path was traced to check the energy profiles connecting each TS with the two associated minima of the proposed mechanism by using the second-order González−Schlegel integration method.[27] The electronic structures of stationary points were analyzed by the natural bond orbital method.[28] All calculations were carried out with the Gaussian 03 suite of programs.[29]

Acknowledgment. Financial support from the Spanish Goverment (Grant No. CTQ2004-03811), the Generalitat Valenciana (Grupos 03/82), and the Universidad Politécnica de Valencia (Grant 20060286 and fellowship to E.A.L.) is gratefully acknowledged.

Supporting Information Available: The (U)B3LYP/6-31G* computed total energies, $\langle S^2 \rangle$ values, unique imaginary frequency of the TSs, and Cartesian coordinates of the stationary involved in the reactions of the 1,5- and 1,4-azabiradicals **Ia** and **Ib** (23 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

JO0601967

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