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Heterocyclic Photochemistry in Contrast with Carbon Behavior. Regioselective Photochemical Rearrangement of an Azacyclohexadienone: Mechanistic and Exploratory Organic Photochemistry[1]

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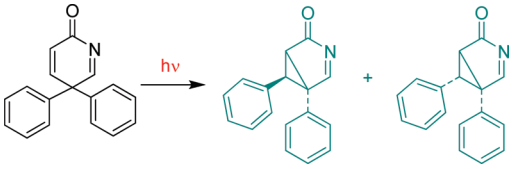
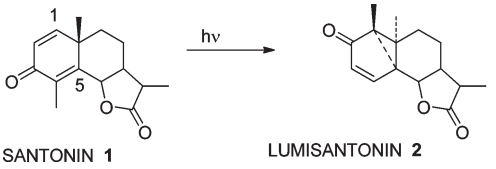


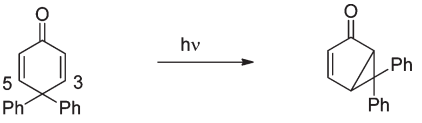
The Type-A photochemistry of cyclohexadienones is well-studied and follows a well-established mechanistic pathway. One early example is the rearrangement of santonin to lumisantonin. Another example is the rearrangement of 4,4-diphenylcyclohexa-1,5-dienone. Remarkably, replacement of one carbon by nitrogen alters the reaction course to give a regioselective phenyl migration.

Introduction

5,5-Disubstituted 2,5-cyclohexadienones undergo a facile rearrangement from the triplet. A very early example was the rearrangement of santonin (**1**) to lumisantonin (**2**) (note eq 1).[2] In 1961, the mechanism was established,[3] and the example of the 4,4-diphenyl-2,5-cyclohexadienone (**3**) rearrangement to bicyclo[3.1.0]hexenone (**4**) was presented[3] (note eq 2). These reactions proceed by initial β,β-bonding

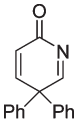


SANTONIN **1** LUMISANTONIN **2** (1)



3 **4** (2)

(i.e., 1,5 in santonin and 3,5 in the diphenyldienone) and are reactions of the n$-\pi^*$ triplets. It was of basic interest to ascertain the effect of replacing one ring carbon by nitrogen as in the azacyclohexadienone (**5**).



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Results

Synthesis of Photochemical Reactants and Potential Products. The synthesis of 5,5-diphenylpyridin-2(5*H*)-one (**5**) was carried out as described in Scheme 1. A starting point was the known[4] cyano-aldehyde (**6**). The latter had been reported to be converted to the diphenylazacyclohexenone (**10**) by Cragoe[4a] in 1958 by heating with sulfuric acid in acetic acid. However, the repetition of the procedure led to a compound with inconsistent proton and carbon NMR spectra. Instead, the compound proved to be pyridone (**12**) resulting from a rearrangement discussed below.

Utilizing the same cyanoaldehyde (**6**) and the sequence in Scheme 1, the desired aza-enone (**10**) was obtained and with a melting point not too far (170 vs 174 °C) from that of **12**. The

(1) (a) Publication 287. (b) For Publication 286, see: Zimmerman, H. E., *J. Org. Chem.*, **2008**, *73*, 1247-1251. (c) For Publication 285, see: Zimmerman, H. E.; Suryanarayan, V., *Eur. J. Org. Chem.*, **2007**, *72*, 4091-4102.

(2) (a) Arigoni, D.; Bosshard, H.; Bruderer, H.; Büchi, G.; Jeger, O.; Krebaum, L. J. *Helv. Chim. Acta* **1957**, *40*, 1733–1748. (b) Barton, D. H. R.; DeMayo, P.; Sahfiq, M. *J. Chem. Soc.* **1958**, 140–145.

(3) (a) Zimmerman, H. E. *17th National Organic Symposium of the American Chemical Society, Abstracts*, Bloomington, IN, 1961, pp 31−41. (b) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527–4540.

(4) (a) Cragoe, E. J.; Pietruszkiewicz, A. M.; Robb, C. M. *J. Org. Chem.* **1958**, *23*, 971–980. (b) Beard, C.; Burger, A. *J. Org. Chem.* **1962**, *27*, 1647–1650.

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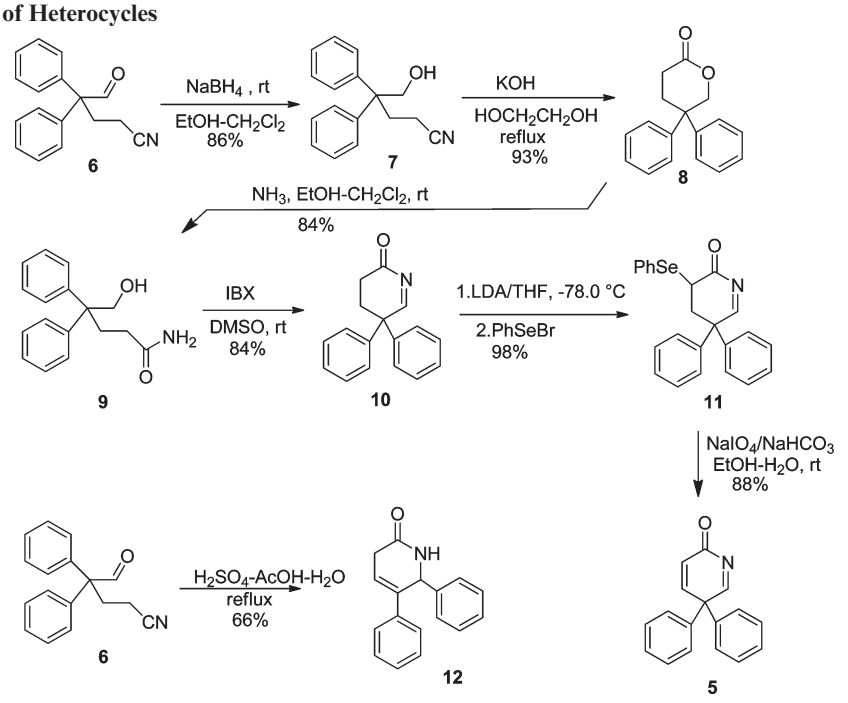
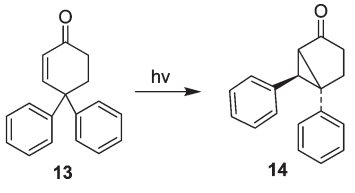
SCHEME 1. Synthesis of Heterocycles



structures of compounds **10** and **12** were established from the NMR (^{1}H, ^{13}C, DEPT, C,H-COSY, GHMBC, and homonuclear decoupling); note the Experimental Section. Aza-cyclohexenone (**10**) was then converted to the desired aza-cyclohexadienone (**5**).

Details are given in the Experimental Section for the sequences **9** to **5** and **9** to **12**. The remaining conversions are given in the Supporting Information.

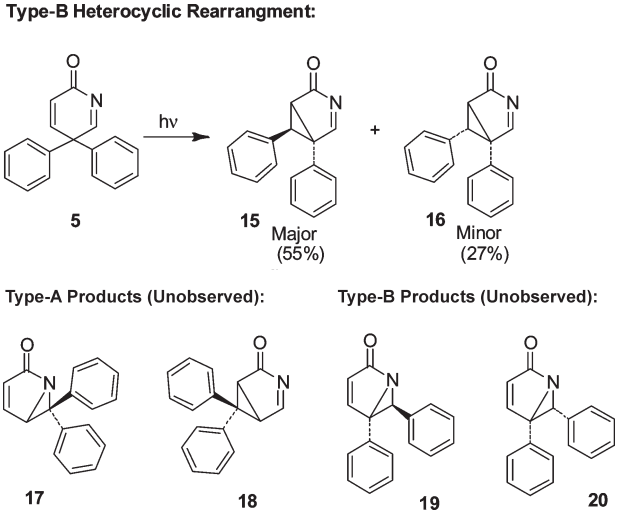
Photochemical Results. The photochemistry proved to be quite unusual and reminiscent of carbocyclic enone reactivity (note eq 3).[5] The aza-cyclohexadienone behavior is outlined in Scheme 2. The Type-A photoproducts, common in a myriad of all-carbon examples,[3] went unobserved. Instead, two bicyclic Type-B[5] rearrangement products were formed. The structures of compounds **15** and **16** were established from the NMR (^{1}H, ^{13}C, DEPT, COSY, and NOESY) with consideration of the AB methine coupling and also the downfield imine hydrogen signal; note the Experimental Section and Supporting Information again.



(3)

Beyond this, there was encountered regioselectivity in which phenyl migration was to the terminus of the carbon to carbon π-system rather than the imine one. However, as in all-carbon Type-B photochemistry[5] there

SCHEME 2. Photochemical Results: Type-B Heterocyclic Products, Regioselectivity, Stereochemistry, And Lack of the Common Type-A Photochemistry So Characteristic of Dienone Reactivity

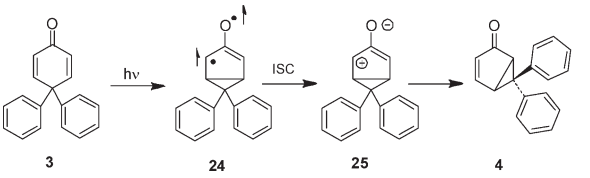


was a preference for the endophenyl stereochemistry (i.e., **15** vs **16**). And, it is seen from a theoretical stand point that the Type-B preference is understandable (vide infra).

Theoretical and Computational Results. As noted, the curious aspect of the photochemistry was the preference for the Type-B reaction course rather than the ubiquitous Type-A. Thus, we carried out computations with Gaussian 03, using density functional theory, namely b3lyp/6-31g*. The triplets were geometry optimized since they were the initially formed species. The singlets (i.e., S_0) were given the geometry of the triplets from whence they derive. Interestingly in the case of the Type-A species **23** the energy with an S_0 configuration proved

(5) (a) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036–4042. (b) Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2033–2047. (c) Zimmerman, H. E.; Kutateladze, A. G. *J. Org. Chem.* **1995**, *60*, 6008–6009.

higher than that of the corresponding triplet. However, this species had the geometry of the triplet and was unrelaxed. Geometry optimization led to an energy close to that of the triplet (−785.479) but the process also led further to three-ring-opening without a local minimum being obvious. The experimental evidence suggests that this zwitterionic species is not reached in the photochemistry. This differs from the carbocyclic dienone rearrangement[3] illustrated in eq 4.



(4)

TABLE 1. Energies of Reactants, Intermediate Species, and Products

	singlets	triplets	singlets	triplets
Type-B (N)			Type-B (M)	
dienone **5**	−785.5737	−785.4661	−785.5737	−785.4661
Spiro[a] **21**, **22**	−785.4912	−785.4571	−785.4706	−785.4706
endo bicyclic **15**, **19**	−785.5539	−785.4266	−785.5399	−785.4622
Type-A[b] (N)			Type-A (M)	
dienone **5**	−785.5737	−785.4661	−785.5737	−785.4661
Type-A **23**	−785.4584	−785.4789	−785.4584	−785.4789
DiPhC[c] **17**, **18**	−785.5539	−785.4430	−785.5625	−785.4607

[a] Spiro is the phenyl-bridged diradicals. [b] Type-A is the 3,5-bridged species. [c] DiPhC is the Type-A rearranged bicyclic. Energies in hartrees (627.5 kcal/mol per hartree).

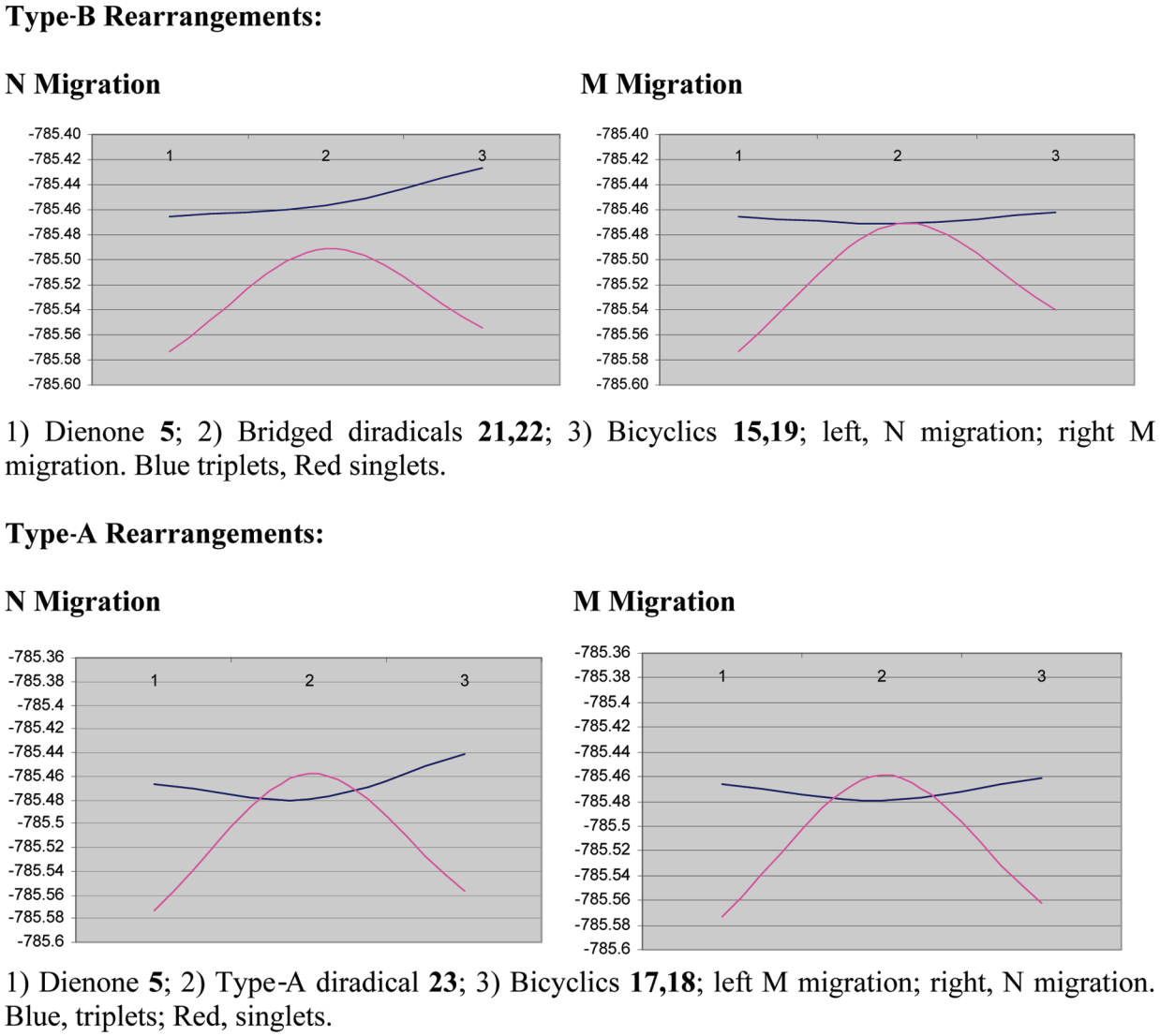
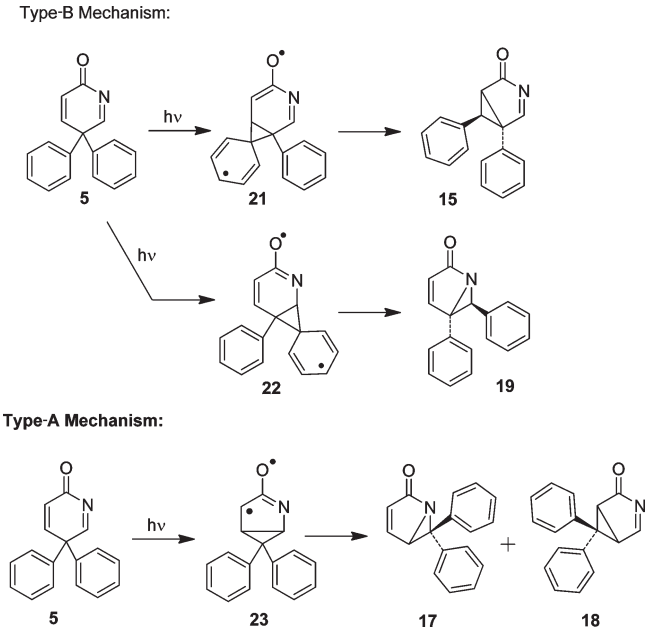


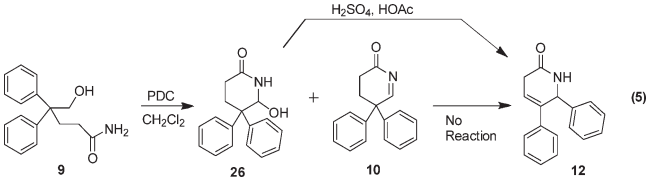
FIGURE 1. Type-A and Type-B rearrangement energy diagrams.

SCHEME 3. Possible Rearrangements: Type-A and Type-B



Discussion

In a brief diversion we note that the rearrangement encountered by Cragoe proved not to be a reaction of aza enone **10** but, rather, a reaction of its precursor **26**. See eq 5.



In the aza-dienone photochemistry the singlet and triplet energies of one reactant, four a priori photoproducts, and three intermediates were considered computationally (see Table 1). This is shown graphically in Figure 1. It then becomes possible to compare theory with reality.

The reactions for which the computations done for the Type-A and for the Type-B rearrangements, as described above, are now outlined in Scheme 3. In both instances, rearrangements involving the nitrogen side of the heterocycle (Type N) and the side distant from nitrogen (Type M) were a priori possible. The energies obtained, and listed in Table 1, are now utilized in considering the relative preferences of the four reaction pathways as discussed below. Throughout the correlation assumes the unrelaxed S_0 species.

Turning to consideration of Figure 1, we note that for the Type-A rearrangement, the triplets (blue) intersect the ground state (i.e., S_0) surfaces before the S_0 singlets (red) reach a maximum. Hence, one can anticipate intersystem crossing and reversion to reactants. In contrast, in the all-carbon Type-A rearrangement intersystem crossing of the 3,5-bridged triplet leads to a zwitterion (note eq 4). In the present case this species is clearly not reached (vide infra).

In the case of the aza-Type-B process, with migration to the distant (i.e., M) side of the heterocycle there is an essential degeneracy between T_1 and S_0 and anticipated intersystem crossing (T_1 to S_0) with product formation. In contrast, for the N migration, i.e., on the nitrogen side of the heterocycle, the T_1-S_0 intersection is lacking and intersystem crossing is much less likely. Thus, the experimentally observed Type-B rearrangement with a preference for the M migration (i.e., distant from nitrogen) is in accord with the computational prediction.

It is clear that the reaction course is not controlled by relative excited-state energies for alternative pathways. Thus, three of the reactions begin as triplets reacting exothermically while the nonobserved Type-B (N-migration) pathway begins on a upward energy path, and we see that there is no correlation with energetics. The reaction course is controlled by a requirement for a T_1-S_0 intersection which does not occur on the portion of the S_0 surface leading back to reactant. This requirement is fulfilled only by the Type-B "M-migration" (i.e., the top right scheme in Figure 1). Interestingly, the heterocyclic photochemistry of the aza-dienone parallels that of the all-carbon cyclohexenone as depicted in eq 3.

Conclusion

The surprising result in this study, which a priori would not have been predicted, is the lack of Type-A rearrangement so characteristic of 4,4-disubstituted cyclohexadienones. It is thus seen that the photochemistry of nitrogen heterocycles cannot be assumed to parallel that of the corresponding all carbon reactants and promises to afford new reactivity. The naive assumption that organic photochemistry is a mature field would then lead to loss of exciting new results.

Experimental Section

5-Hydroxy-4,4-diphenylvaleramide (9). To a stirred solution of 14.0 g (55.5 mmol) of 5,5-diphenylvalerolactone (**8**) in 150 mL of methanol and 50 mL of dichloromethane was added dropwise ca. 25 mL of liquid ammonia. The reaction mixture was stirred for 24 h at room temperature. Solvent was then removed in vacuo and the residue recrystallized from chloroform: yield 12.6 g (84%); mp 136−138 °C; ^{1}HNMR (300 MHz, $CDCl_3$) δ 2.00 (t, 2H, J = 7.5 Hz), 2.47 (br s, 1H), 2.55 (t, 2H, J = 7.5 Hz), 4.11 (s, 2H), 5.50 (br s, 1H), 5.63 (br s, 1H), 7.16−7.32 (m, 10H); ^{13}CNMR (75 MHz, DMSO-d_6) δ 31.1; 31.5; 51.1; 67.0; 126.3; 128.4; 128.5; 147.3; 175.2; HRMS (EI) Calcd for $C_{17}H_{19}NO_2^+$ ([M^+]) 269.1411, found 269.1410.

5,5-Diphenyl-3,4-dihydro-2(5)-pyridone (10). *(Caution! Due care should be exercized when working with IBX, since the compound is shock- and heat-sensitive!).* To solution of 30.0 g (0.11 mol) of 2-iodoxybenzoic acid[6] (IBX) in 400 mL of DMSO was added 10.92 g (40.5 mmol) of 5-hydroxy-4,4-diphenylvaleramide (**9**). The reaction mixture was stirred for 6 days at room temperature, poured into 2000 mL of water, and extracted with ethyl acetate (5 × 200 mL). The combined organic phase was washed with water (3 × 400 mL) and dried over sodium sulfate and the solvent removed in vacuo. The residue was recrystallized from 2-propanol: yield 6.75 g; mp 169−170 °C. The mother liquor was concentrated in vacuo and the residue purified by column chromatography (15 × 4 cm) with hexane−ethyl acetate (2/1) as eluent. Fractions containing product were combined and concentrated: yield 1.7 g; mp 168−170 °C; total yield 8.45 g (84%); ^{1}HNMR (300 MHz, DMSO-d_6) δ 2.31 (t, 2H, J = 6.3 Hz), 2.76 (t, 2H, J = 6.3 Hz), 7.12−7.16 (m, 4H), 7.26−7.38 (m, 6H), 11.09 (s, 1H); ^{13}CNMR (75 MHz, DMSO-d_6) δ 30.2,

(6) Frigerio, M.; Santagostino, M.; Sputore, S. *J. Org. Chem* **1999**, *64*, 4537–4538.

30.3, 56.7, 127.9, 128.7, 129.0, 141.8, 173.2, 175.5; HRMS (EI) calcd for $C_{17}H_{15}NO^+$ ([M^+]) 249.1149, found 249.1160.

3-Phenylselenyl-5,5-diphenyl-3,4-dihydro-2(5)pyridone (11). A solution of 2.33 g (23 mmol) of diisopropylamine into 15 mL of anhydrous THF was cooled to −70 °C in an atmosphere of argon. Then 15.0 mL (23 mmol) of 1.55 M *n*-butyllithium in hexane was added via syringe over 1 min. The reaction mixture allowed to warm to 0 °C and then cooled back to −70 °C. Thereafter, a solution of 2.3 g (9.2 mmol) of 5,5-diphenyl-3,4-dihydro-2(5)-pyridone (**10**) in 15 mL of anhydrous THF was added dropwise and the reaction mixture stirred for 1.5 h at −70 °C; a yellow stirrable suspension was formed. A solution of phenylselenium bromide, prepared by addition of 1.84 g (11.5 mmol) of bromine to a stirred solution of 3.6 g (11.5 mmol) of diphenyldiselenide to 15 mL of anhydrous THF, was rapidly added via syringe. The solution rapidly became colorless. The reaction mixture was allowed to warm to room temperature, poured into mixture of 700 mL of water and 10 mL of concd HCl, and extracted with ethyl acetate (4 × 250 mL). The combined organic phase was washed with water (3×150 mL) and brine (150 mL) and dried over sodium sulfate and the solvent removed on a rotary evaporator. The residue was purified by column chromatography (45×4 cm) using hexane−ethyl acetate (3/1) as eluent. Fractions containing product were combined and concentrated in vacuo, and the product was recrystallized from 2-propanol: yield 3.66 g (98%); mp 165−167 °C; ^{1}HNMR (300 MHz, $CDCl_3$) δ 2.83 (dd, 1H, J=5.1 and 14.1 Hz), 2.96 (t_{app}, 1H, J=14.4 Hz), 3.98 (dd, 1H, J= 5.1 and 12.3 Hz), 6.91−6.94 (m, 2H), 7.09−7.13 (m, 2H), 7.22−7.40 (m, 9H), 7.55−7.58 (m, 2H), 8.07 (s, 1H). Partial homonuclear decoupling with saturating spin states of the PhSeC*H* proton leads to simplification of spectra and doublet of doublets at δ 2.83 (one proton of the adjacent diastereotopic CH_2 group which is *cis* to the PhSeC*H* proton**)** along with a triplet at δ 2.96 (the other proton from the adjacent diastereotopic CH_2 group which is *trans* to the PhSeC*H* proton) both collapse to a doublet of doublets at δ 2.83 and 2.96 with true J values of −14.1 Hz (geminal) and 1.8 Hz (probably long-range coupling to imine C*H* proton): ^{13}CNMR (75 MHz, $CDCl_3$) δ 39.3, 39.6, 58.1, 126.7, 127.7, 127.8, 128.4, 128.5, 128.6, 129.1, 129.5, 129.6, 136.0, 137.7, 141.8, 170.9, 173.9.

5,5-Diphenylpyridin-2(5*H*)-one (5). To a suspension, cooled to 0 °C, of 6.6 g (16.3 mmol) of 3-phenylselenyl-5,5-diphenyl-3,4-dihydro-2(5)pyridone (**11**) in 850 mL of ethanol was added to a solution of 1.71 g (20.3 mmol) of sodium bicarbonate in 170 mL of water followed by 8.72 g (40.7 mmol) of solid sodium periodate. The cooling bath was removed, and the reaction mixture, a milky suspension, was stirred for 48 h at room temperature, poured into 3500 mL of water, and extracted with dichloromethane (5 × 250 mL). The combined organic phase was washed with saturated sodium bicarbonate solution (1 × 1000 mL) and water (2×1000 mL), dried with sodium sulfate, and concentrated in vacuo. The residue was purified by column chromatography (16 × 5.5 cm) using hexane−ethyl acetate (9/1) to elute the diphenyl diselenide (from disproportionation of phenylseleneninic acid) and then hexane−ethyl acetate (1.5/1) mixture to elute the crude product (3.65 g), which was recrystallized from heptane−toluene (1/1): yield 3.20 g; mp 174−177 °C. Concentration of the mother liquor from crystallization followed by column chromatography (3 × 15 cm) with hexane-ethyl acetate (3/1) afforded an additional 0.4 g of product which was recrystallized from heptane−toluene (1/1): yield 0.34 g; mp 174−177 °C; overall yield 3.54 g (88%); ^{1}HNMR (300 MHz, $CDCl_3$) δ 6.29 (dd, 1H, J=2.1 and 10.2 Hz), 7.05 (d, 1H, J= 10.2 Hz), 7.23−7.39 (m, 10H), 8.48 (s, 1H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 59.9, 118.9, 128.4, 128.8, 129.1, 140.6, 150.7, 164.8, 173.3; HRMS (EI) calcd for $C_{17}H_{13}NO^+$ ([M^+]) 247.0992, found 247.0986.

6-Hydroxy-5,5-diphenyl-2-piperidone (26). To a suspension of 600 mg (2.2 mmol) of 5-hydroxy-4,4-diphenylvaleramide (**9**) in 25 mL of dichloromethane was added 1.25 g (3.3 mmol) of pyridinium dichromate. The reaction mixture was stirred for 3 h at room temperature and filtered through a short column (1× 4 cm), and the silica gel was washed with 100 mL of ethyl acetate. The filtrate was concentrated in vacuo and the dark residue weighing 430 mg was purified by column chromatography (1× 25 cm). Initially an 8/1 mixture of hexane and ethyl acetate was used, and 10 mg of benzophenone was eluted. Then 3.5/1 hexane−ethyl acetate eluted 35 mg of 5,5-diphenylvalerolactone (**8**) followed by 86 mg of 5,5-diphenyl-3,4-dihydro-2(5)-pyridone (**10**). Then pure ethyl acetate was employed, and 6-hydroxy-5,5-diphenyl-2-piperidone **(26)** was eluted: yield 230 mg (39%); mp 193−195 °C dec (from chloroform); ^{1}HNMR (300 MHz, DMSO-d_6) δ 1.64 (m, 1H), 2.19 (dd, 1H, J = 4.8 Hz and 18 Hz), 2.42−2.50 (m, 1H), 2.84 (m, 1H), 5.49 (t, 1H, J= 4.8 Hz), 5.76 (d, 1H, J= 6.0 Hz), 7.07−7.29 (m, 10H), 8.27 (d, 1H, J = 4.2 Hz); ^{13}CNMR (75 MHz, DMSO-d_6) δ 24.7, 29.4, 49.6, 78.7, 126.1, 126.6, 127.8, 128.0, 128.5, 128.9, 144.8, 147.0, 170.4; HRMS (EI) calcd for $C_{17}H_{17}NO_2^+$ ([M^+]) 267.1254, found 267.1260.

Rearrangement of 6-Hydroxy-5,5-diphenyl-2-piperidone (26) into 5,6-Diphenyl-4,5-dehydro-2-piperidone (12). A mixture of 500 mg (1.8 mmol) of 6-hydroxy-5,5-diphenyl-2-piperidone (**26**), 1.0 mL of concd sulfuric acid, 4.0 mL of glacial acetic acid, and 1.0 mL of water was refluxed for 2 h. The mixture was then poured, with stirring, into 100 mL of cold water and extracted with dichloromethane (4×25 mL). The combined organic phase was washed with water (3×15 mL), dried with sodium sulfate, and concentrated in vacuo. The residue was purified by column chromatography (10×1 cm) with ethyl acetate as eluent: yield 220 mg (47%); mp 172−174 °C (from ethyl acetate).

Photolysis of 5,5-Diphenylpyridin-2(5*H*)-one. A solution of 1.3 g (5.2 mmol) of 5,5-diphenylpyridin-2(5*H*)-one (**5**) in 300 mL of dry benzene was purged with oxygen free nitrogen for 1 h. Then the reaction mixture was irradiated with a 400 W medium pressure mercury lamp. After 45 min, the ^{1}HNMR showed complete consumption of starting material. Concentration in vacuo and chromatography (17×2 cm) with hexane-ethyl acetate (5/1) as an eluent afforded two compounds. Compound **15**: yield 0.71 g (55%); mp 165−167 °C (from 2-propanol); ^{1}HNMR (300 MHz, DMSO-d_6) δ 3.32 (d, 1H, J= 9.0 Hz), 3.55 (d, 1H, J= 9.0 Hz), 7.32−7.42 (m, 8H), 7.60−7.63 (m, 2H), 10.55 (br s, 1H); ^{13}CNMR (75 MHz, CD_3OD) δ 33.6, 41.7, 43.2, 127.9, 128.1, 128.6, 128.7, 129.1, 129.2, 133.6, 174.6, 175.5; HRMS (EI) calcd for $C_{17}H_{13}NO^+$ ([M^+]) 247.0992, found 247.0988. Compound **16**: yield 0.36 g (27%); mp 222−225 °C (from 2-propanol); ^{1}HNMR (300 MHz, DMSO-d_6) δ 3.49 (d, 1H, J = 3.6 Hz), 3.79 (d, 1H, J=3.6 Hz), 6.98−7.01 (m, 2H), 7.07−7.11 (m, 3H), 7.18−7.28 (m, 5H), 10.91 (br s, 1H); ^{13}CNMR (75 MHz, CD_3OD) δ 31.1, 43.2, 44.2, 127.2, 127.9, 128.0, 128.8, 131.1, 133.8, 176.0, 176.6; HRMS (EI) calcd for $C_{17}H_{13}NO^+$ ([M^+]) 247.0992, found 247.0988.

NMR Evidence for Structure and Stereochemistry Elucidation for Photoproducts (15) and (16). The structures of compounds **15** and **16** were assigned by NMR spectroscopy. ^{13}C NMR of both compounds along with DEPT (90) and DEPT (135) data indicate presence of two C=X groups (signals around δ 175, carbonyl and imine carbons), two aromatic quaternary and six aromatic CH carbons, two CH methine carbons, and one aliphatic quaternary carbon. This does not fit structures of compounds **17**, **19**, and **20** since each of them must have only one downfield signal from a C=X group, eight aromatic signals, one signal from aliphatic CH carbon, one signal from quaternary aliphatic carbon, and two downfield signals from vinylic CH carbons from the CH=CH− double bond conjugated with the carbonyl group. The ^{1}H NMR of compound **15** has two doublets at δ 3.32 and 3.55 with vicinal coupling constant ^3J = 9 Hz,

which correspond to ca. 30° dihedral angle between two cis methine protons; this fits well for both compounds **15** and **18**. If compound **18** were involved the proton from the CH group bonded to the imine CH=N group should be split and appear as a doublet of doublets due to additional coupling to imine C*H* proton (ca. $J = 3$ Hz). This is not observed (absence of coupling was also confirmed by COSY). Further proof of structure of **15** derived from a NOESY experiment which did not indicate proximity of any of the aliphatic protons to imine C*H* proton. The ^{1}H NMR of compound **16** has two doublets at δ 3.49 and 3.79 with vicinal coupling constant $^3J = 3.6$ Hz, corresponding[7] to ca. 110° dihedral angle between two aliphatic protons. That geometry only fits compound **16**. In both of the ^{1}H spectra of compounds **15** and **16** there are downfield singlets around δ 10.9 from imine C*H* protons, which would not be observed in case of compounds **17**, **19**, and **20**. In addition, the ^{1}H NMR of compounds **15** and **16** lacks signals from vinylic protons as would be the case of compounds **17**, **19**, and **20**. Finally the HRMS of both compounds 15 and **16** were in agreement with their molecular formulas.

(7) (a) MestRec-J Programming. (b) Haasnot, C. A. G.; de Leeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2792. (c) Smith, W. B.; Barfield, M. *Magn. Reson. Chem.* **1993**, *31*, 696.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.