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The Aza-Type-B Photochemical Rearrangement: The Role of a Second Carbonyl in Heterocyclic Photochemistry. Mechanistic and Exploratory Organic Photochemistry[1,2]

Howard E. Zimmerman* and Oleg D. Mitkin

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

zimmerman@chem.wisc.edu

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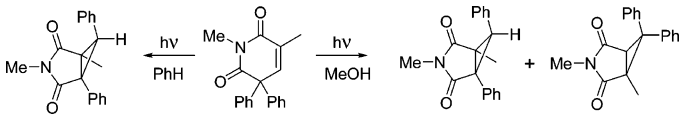
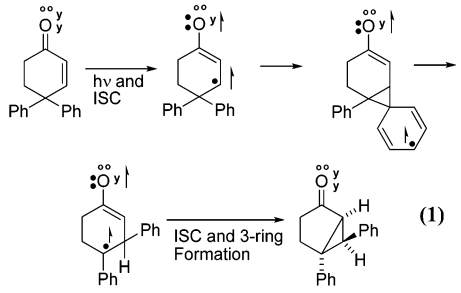
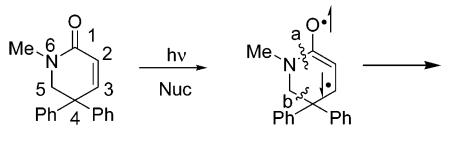


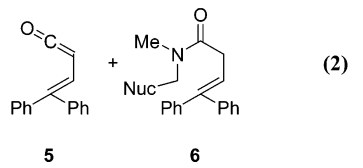
In contrast to the photochemistry of monocyclic aza-cyclohexenones, their counterparts with a second carbonyl group undergo photochemical rearrangements which parallel those of the 4,4-disubstituted cyclohexenones.

Introduction

One of the better known organic photochemical rearrangements is that of 4,4-disubstituted cyclohexenones.[3] Note eq 1



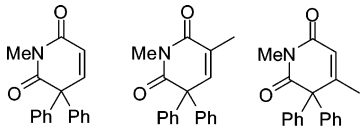




which includes the mechanism. Surprisingly, replacement of the C-6 carbon by an amino nitrogen has been found[2] to effect quite different reaction courses. One example is shown in eq 2. Interestingly, it now has been found that introduction of a second carbonyl group leads to type-B type photochemistry, and it is that chemistry which we now describe.

Results

Synthesis of Photochemical Reactants. The three reactants selected for study were diphenylpyridine-2,6-diones **7**, **8**, and **9**. The first was prepared in a single step from the imide **10** as noted in Scheme 1, and the second, **8**, utilized the short sequence in the same scheme using a modified Reich procedure for introduction of the conjugation.[4] Both synthetic reactants **10** and **11** were known.[5,6]



The third photochemical reactant **9** was prepared as outlined in Scheme 2, utilizing photochemical *cis-trans* isomerization. The ratio of **16**/**17** was 53:34 (360 nm light).

(1) This is Paper 283 of our general series.

(2) (a) For Paper 282, see: Zimmerman, H. E. *Pure Appl. Chem.* **2006**, 2193−2203. Porter Award Address. (b) For Paper 281, see: Zimmerman, H. E.; Mitkin, O. *J. Am. Chem. Soc.* **2006**, *128*, 12743−12749.

(3) (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.; Hancock, K. G. *J. Am. Chem. Soc.* **1968**, *90*, 3749−3760.

(4) Reich, H. J. *Org. Synth.* **1980**, *59*, 58−65.

(5) Urech, E.; Tagmann, E.; Sury, E.; Hoffmann, K. *Helv. Chim. Acta* **1953**, *36*, 1809−1815.

(6) Bretschneider, H.; Deutscher, H.; Klotzer, W.; Sander, M. *Monatsh. Chem.* **1958**, *89*, 288−300.

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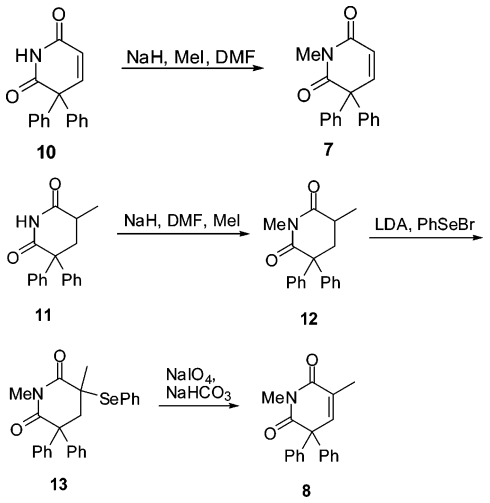
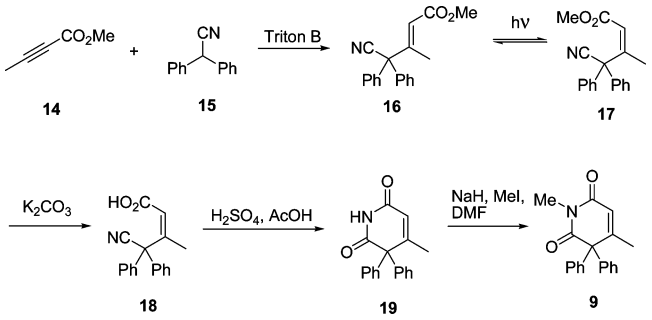
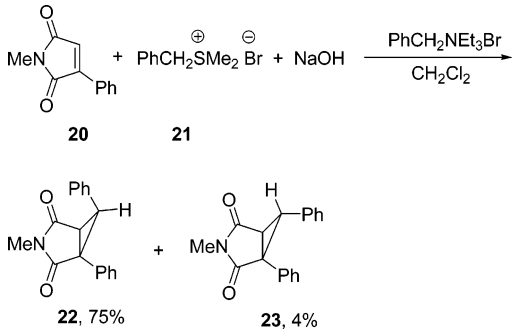
SCHEME 1. Synthesis of Two of the Photochemical Reactants



SCHEME 2. Synthesis of the Third Photochemical Reactant 9



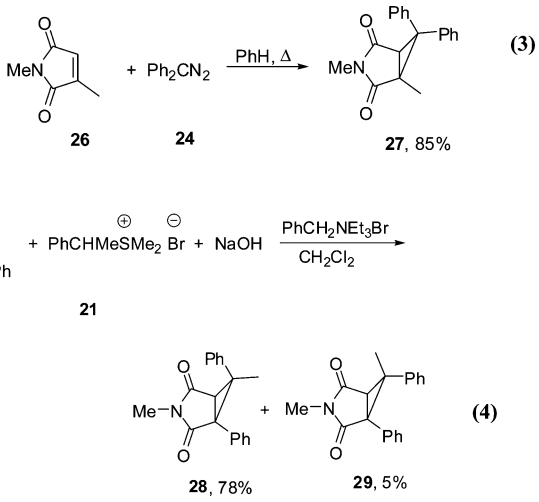
SCHEME 3. Synthesis of Potential Photoproducts



Synthesis of Potential Photochemical Products. In this study, a number of bicyclic[3.1.0] heterocycles were encountered, and it was expedient to synthesize a number of potential photoproducts independently. These syntheses are outlined in Scheme 3. Where further photoproducts resulted, we dealt with each structure individually.

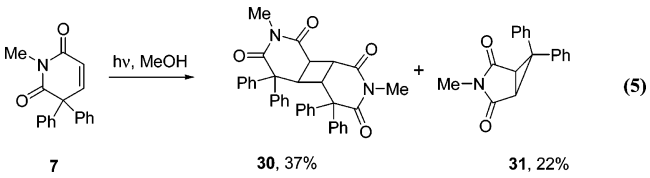
From the known reactant **20**,[7] isomers **22** and **23** were obtained and distinguished based on their cyclopropane ring proton ^{1}H NMR splitting constants: 8.4 Hz for the *endo* bicyclic **22** and 3.5 Hz for the *exo* bicyclic **23**, which is in agreement with an earlier study of similar systems.[3a] Also, the protons of the *N*-methyl group of *endo*-**22** exhibit an upfield shift to δ 2.44 compared with δ 3.00 in *exo*-**23** due to shielding by the phenyl group.

Using diphenyldiazomethane **24** with the imide **26**,[8] bicyclic **27** was obtained. Bicyclic products **28** and **29** were obtained from the known[7] **20**. The assignment of *exo* and *endo* configurations was based on an upfield shift of *N*-methyl group protons to δ 2.33 in *endo* compound **28** compared to δ 2.99 in *exo*-**29**.

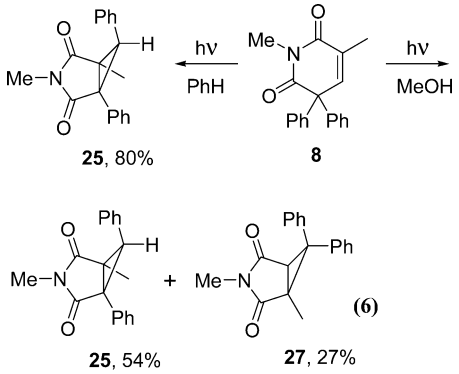


The Photochemistry. On photolysis of reactant **7** in methanol, we observed two photoproducts, **30** and **31**. Bicyclic product **31** is a known[9a] compound, and dimer **30** is assigned the anti head-to-head structure **30** on the following grounds. Since the ^{13}C NMR spectrum showed only eight signals, unsymmetrical structures can be ruled out. Structures with two *trans*-cyclobutane ring junctions can also be eliminated. On the basis of excessive crowding a *cis-syn-cis* dimer appears to be unlikely. In the protium NMR, a downfield signal at 3.41 pm (d, $J = 8.6$ Hz) is assigned to bridgehead protons α to the carbonyl; a head-to-tail structure would not be expected to give a sharp doublet.[6]

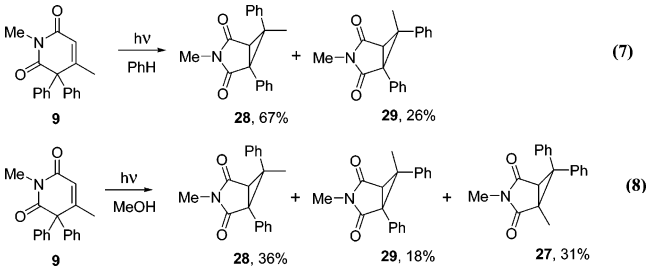
The photolysis of the heterocycle **8** in benzene afforded



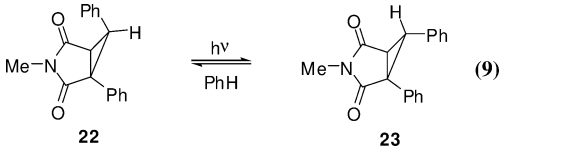
exclusively the type-B rearrangement product **25**, whereas in methanol **27**, a type-A structure[9b] was also formed. The structure of **25** was established by X-ray.[10]



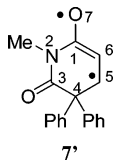
The photolysis of reactant **9** in benzene afforded *endo* and *exo* type-B photoproducts. See eq 7. However, again, in methanol, type-A rearrangement also resulted to give **27** (eq 8).



The formation of both diastereomers from **9** contrasts with the formation of only *endo*-**25** from irradiation of **8**. Compare eqs 6 and 7. This appears to result from the reluctance of **25** to isomerize. In a further search for bicyclic stereoisomerization, **22** was photolyzed and smoothly led reversibly to its stereoisomer **23**. See eq 9.



Computational Aspects and Methodology. In parallel with our experimental efforts, and in order to better understand the reaction course, we turned to ab initio computations. CASSCF-(8,8)/6-31G(d) computations and NBO analyses on compound **7** showed that the lowest Franck−Condon triplet excited state formed (i.e., with S_0 geometry) is $\pi-\pi^*$. Such triplets are known to result in [2 + 2] additions.[5] The second excited state and relatively close in energy is an $n-\pi^*$ triplet, which is usually responsible for aryl migration. Interestingly, in another set of computations, with T_1 optimized geometry, T_2 exhibited two roots, both with odd-electron densities at carbon-5. Note Table 1. The matching odd-electron density was at oxygen-7, either in the π-system or in the p_y-orbital, depending on the state.



Discussion

Contrast of the Triplet Chemistry with the Second Carbonyl Present. A first item to be noted is the contrast observed between the photochemistry encountered in the present dicarbonyl systems and the photochemistry of the monocarbonyl compound counterparts we had investigated in our earlier studies.[2b] Thus we now see phenyl migration occurring as the prevailing reaction in the dicarbonyl systems in contrast to the bond scission found in the earlier monocarbonyl systems. Contrast eqs 1 and 2. The bond scission chemistry was shown to arise from the singlet excited states[2] while it is the triplet which is responsible for the chemistry of the present research, even without the use of a triplet sensitizer. It is clear that the second carbonyl enhances intersystem crossing as a result of greater spin−orbit coupling. While the monocarbonyl compounds are amides with diminished spin−orbit coupling, the imide structure of the dicarbonyl compounds reverses this effect and partially restores the individual carbonyl π-bond orders, thus increasing the spin−orbit coupling and hence the rapid conversion to triplets.

A related observation is the appearance of the oxa-di-π-methane rearrangement when the solvent is methanol. Structurally, the reaction is analogous to the type-A rearrangement. However, oxa-di-π-methane rearrangements occur via the $\pi-\pi^*$ excited state, and here, methanol is seen to raise the energy of the $n-\pi^*$ state, thus permitting intervention of $\pi-\pi^*$ reactivity.

TABLE 1. Energies and Densities for Triplet Eigenvalues 1 and 2[a]

	Eigenvalue 1	Eigenvalue 2
Energy:	−513.49722	−513.49511
Densities:		
C5	1.02229	1.01204
O-p π	1.91036	1.05782
p_y	0.99535	1.86219

[a] NBO densities are occupancies from natural orbitals as a basis.

Conclusion

The course of the photochemistry of the nitrogen heterocycles has proven to be dependent on the number of carbonyl groups. With one carbonyl, singlet photochemistry has been shown to result. In contrast, with a second carbonyl, intersystem crossing is enhanced and triplet chemistry is observed. In addition, the reaction course is solvent dependent. This dependence controls whether it is the $n-\pi^*$ or the $\pi-\pi^*$ triplet which reacts. Computationally, the two states were determined to be close-lying. In benzene, the type-B rearrangement, common in cyclohexenone photochemistry, resulted from the $n-\pi^*$ triplet. In methanol, there is competitive oxa-di-π-methane rearrangement which occurs as expected from the $\pi-\pi^*$ triplet.

Experimental Section

1-Methyl-5,5-diphenylpyridine-(1*H*,5*H*)-2,6-dione (7). A 230 mg (5.8 mmol) portion of sodium hydride (60% in mineral oil) was washed free of oil with hexane and THF and suspended in 15.0 mL of DMF. Then 1.022 g (3.9 mmol) of imide[5] **10** was added with stirring. After the hydrogen evolution was complete (15 min), 0.40 mL (6.4 mmol) of methyl iodide was added and stirring continued overnight. The mixture was diluted with water, extracted with benzene, washed, dried, concentrated in vacuo, and crystallized from heptane to give 963 mg (89.5%) of 1-methyl-5,5-diphenylpyridine-(1*H*,5*H*)-2,6-dione (**7**): mp 125.5−126.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.32−7.39 (m, 6H), 7.21−7.26 (m, 4H), 7.01 (d, J = 10.2 Hz, 1H), 6.34 (d, J = 10.2 Hz, 1H), 3.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 173.45, 164.48, 148.07, 140.88, 128.57, 128.40, 127.85, 199.02, 59.26, 26.40. HRMS calcd for $C_{18}H_{15}NO_2$ 300.1000 (M + Na), found 300.0996 (M + Na).

5-Methyl-3,3-diphenylpiperidine-2,6-dione (11). A mixture of 3.84 g (13.1 mmol) of methyl 4-cyano-2-methyl-4,4-diphenylbutanoate[6] and 2.30 g (16.7 mmol) of potassium carbonate was boiled in a mixture of 5.5 mL of water and 37.0 mL of methanol for 2 h. Methanol was removed under reduced pressure, and the residue was diluted with water, neutralized with hydrochloric acid, extracted

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(8) Gill, G. B.; James, G. D.; Oates, K. V.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1993**, *21*, 2567−2580.
(9) (a) Baltzly, R.; Mehta, N. B.; Russell, P. B.; Brooks, R. E.; Grivsky, E. M.; Steinberg, A. M. *J. Org. Chem.* **1962**, *27*, 213−218. (b) The bicyclic-[3.1.0] photoproduct, geminally substituted with two substituents originally at C-4, is structurally parallel to the type-A photoproducts of 2,5-cyclohexadienones. However, mechanistically, these arise from an oxa-di-π-methane rearrangement as subsequently noted.
(10) The diffractometry was performed by Dr. Ilia Guzei, and we gratefully acknowledge helpful advice from Dr. Ilia Guzei on our Shelxtl computations.

with dichloromethane, dried, and concentrated in vacuo. The residue was dissolved in 15 mL of acetic acid treated with 5.0 mL of sulfuric acid and refluxed for 2 h. After cooling to ambient temperature, the mixture was poured onto crushed ice, and the crude product was filtered and dried. Crystallization from ethanol afforded 2.56 g (70.0%) of 5-methyl-3,3-diphenylpiperidine-2,6-dione: mp 184−186 °C (lit.[6] 183−186 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.00 (br s, 1H), 7.25−7.45 (m, 8H), 7.06−7.09 (m, 2H), 2.66 (d, J = 9.6 Hz, 2H), 2.45 (m, 1H), 1.31 (d, J = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 138.69, 129.30, 128.37, 128.00, 63.83, 21.42. HRMS calcd for $C_{18}H_{15}NO_2$ 300.1000 (M + Na), found 300.1007 (M + Na).

1,5-Dimethyl-3,3-diphenylpiperidine-2,6-dione (12). A 0.55 g (13.8 mmol) portion of sodium hydride (60% in mineral oil) was washed free of oil with hexane and THF and suspended in 20.0 mL of DMF. Then 2.56 g (9.2 mmol) of 5-methyl-3,3-diphenylpiperidine-2,6-dione was added with stirring. After the evolution of hydrogen was complete (0.5 h), 0.86 mL (13.8 mmol) of methyl iodide was added and the stirring continued overnight. The mixture was diluted with water, extracted with benzene, washed, dried, concentrated in vacuo, and crystallized from ethanol to give 1.93 g (71.7%) of 1,5-dimethyl-3,3-diphenylpyridine-(1*H*,3*H*)-2,6-dione: mp 150−151 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.24−7.41 (m, 6H), 7.17−7.20 (m, 2H), 7.07−7.10 (m, 2H), 3.28 (s, 3H), 2.59−2.65 (m, 2H), 2.38−2.50 (m, 1H), 1.32 (d, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 175.36, 174.98, 143.58, 140.23, 129.29, 128.80, 128.15, 128.02, 127.81, 127.45, 57.84, 38.83, 34.64, 27.89, 16.70. HRMS calcd for $C_{19}H_{19}NO_2$ 316.1313 (M + Na), found 316.1322 (M + Na).

1,3-Dimethyl-5,5-diphenyl-3-(phenylselenyl)piperidine-2,6-dione (13). To a solution of 0.90 mL (6.42 mmol) of diisopropylamine in 5.0 mL of THF was added 2.6 mL (6.5 mmol) of 2.5 M *n*-butyllithium in hexane at −70 °C, and the mixture was stirred at −70 °C for 15 min. Then a solution of 1.50 g (5.11 mmol) of the imide in 20 mL of THF was slowly added, and the mixture was stirred for 10 min at −70 °C followed by the addition of preprepared solution of phenylselenyl bromide (obtained by addition of 0.165 mL (3.20 mmol) of bromine to 1.00 g (3.20 mmol) of diphenyldiselenide in 5.0 mL of THF). The mixture was allowed to warm up to room temperature, quenched with saturated ammonium chloride solution, extracted with benzene, washed with brine, dried with sodium sulfate, and concentrated in vacuo. Column chromatography (eluent = hexane/ether 7:1) afforded 2.064 g (90.0%) of 1,3-dimethyl-5,5-diphenyl-3-(phenylselenyl)piperidine-2,6-dione: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.54−7.57 (m, 2H), 7.26−7.45 (m, 9H), 7.03−7.12 (m, 4H), 3.28 (s, 3H), 3.23 (d, J = 15.0 Hz, 1H), 3.05 (d, J = 15.0 Hz, 1H), 1.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 174.66, 173.83, 142.32, 141.90, 138.33, 130.09, 129.17, 129.14, 128.86, 128.36, 128.33, 127.90, 127.82, 57.08, 45.38, 43.55, 28.87, 26.44. HRMS calcd for $C_{25}H_{23}NO_2Se$ 472.0792 (M + Na), found 472.0805 (M + Na).

1,3-Dimethyl-5,5-diphenylpyridine-(1*H*,5*H*)-2,6-dione (8). To a stirred solution of 1.658 g (3.70 mmol) of 1,3-dimethyl-5,5-diphenyl-3-(phenylselenyl)piperidine-2,6-dione and 311 mg (3.70 mmol) of sodium bicarbonate in 55 mL of ethanol was added a solution of 3.166 g (14.8 mmol) of sodium periodate in 18 mL of water with external cooling in an ice bath. The mixture was stirred overnight at ambient temperature, diluted with water, extracted with chloroform, washed with diluted sodium sulfite solution, then with water, dried over sodium sulfate, and the solvent was removed in vacuo to give 0.956 g (88.8%) of 1,3-dimethyl-5,5-diphenylpyridine-(1*H*,5*H*)-2,6-dione **8** after crystallization from ethanol: mp 211−213 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30−7.38 (m, 6H), 7.19−7.22 (m, 4H), 6.75 (dd, J_1 = 3.0 Hz, J_2 = 1.5 Hz, 1H), 3.31 (s, 3H), 2.08 (d, J = 1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 174.15, 165.94, 143.50, 142.03, 128.88, 128.84, 128.07, 126.22, 59.90, 27.20, 16.97. HRMS calcd for $C_{19}H_{17}NO_2$ 314.1157 (M + Na), found 314.1162 (M + Na).

(*E*)-Methyl 4-Cyano-3-methyl-4,4-diphenylbut-2-enoate 16. To 3.73 g (19.3 mmol) of diphenylacetonitrile in 30 mL of dry dioxane were added 2.1 mL (21.2 mmol) of methyl tetrolate at 50−70 °C and then 1.1 mL of Triton B (benzyltrimethylammonium hydroxide 40% solution in methanol). The mixture was refluxed for 2 h, and dioxane was removed under reduced pressure, diluted with water, extracted with ether, washed with diluted hydrochloric acid and brine, dried, and concentrated in vacuo to give 5.518 g (98%) of (*E*)-methyl 4-cyano-3-methyl-4,4-diphenylbut-2-enoate **16**: mp 89−89.5 °C (methanol); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26−7.44 (m, 10H), 5.54 (d, J = 1.2 Hz, 1H), 3.71 (s, 3H), 2.33 (d, J = 1.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 166.42, 155.27, 137.11, 129.20, 128.91, 128.84, 122.47, 121.48, 61.07, 51.62, 18.66.

(*Z*)-Methyl 4-Cyano-3-methyl-4,4-diphenylbut-2-enoate 17. The solution of 5.518 g (18.9 mmol) of the *E* isomer in 250 mL of benzene was purged with nitrogen for 1 h. Irradiation was carried out with the 0.2 M $CuSO_4$ filter solution for 24 h. Separation by column chromatography (column 15.0 cm × 2.5 cm, eluent = hexane/ether 19:1) afforded 2.905 g (52.6%) of the starting *E* isomer and 1.864 g (33.8%) of the desired (*Z*)-methyl 4-cyano-3-methyl-4,4-diphenylbut-2-enoate **17**: mp 91−92 °C (methanol); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33−7.39 (m, 10H), 6.15 (d, J = 1.5 Hz, 1H), 3.28 (s, 3H), 1.90 (d, J = 1.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 165.44, 146.50, 138. 20, 128.87, 128.85, 128.54, 123.19, 121.87, 57.35, 51.53, 25.42.

4-Methyl-5,5-diphenylpyridine-(1*H*,5*H*)-2,6-dione (19). A mixture of 1.864 g (6.4 mmol) of (*Z*)-methyl 4-cyano-3-methyl-4,4-diphenylbut-2-enoate and 1.100 g (8.0 mmol) of potassium carbonate was refluxed in 2.7 mL of water and 18.0 mL of methanol for 2 h. Methanol was removed under reduced pressure, and the mixture was diluted with water, neutralized with hydrochloric acid, extracted with dichloromethane, dried, and concentrated in vacuo. The residue was dissolved in 15 mL of acetic acid treated with 5.0 mL of sulfuric acid and refluxed for 2 h. After cooling to ambient temperature, the mixture was poured onto crushed ice, and the crude product was filtered and dried. Crystallization from propanol-2 afforded 0.753 g (42.4%) of 4-methyl-3,3-diphenylpyridione-2,6: mp 243−246 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.02 (br s, 1H), 7.29−7.39 (m, 10H), 6.28 (s, 1H), 1.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 174.91, 163.90, 159.21, 138.69, 129.30, 128.37, 128.00, 63.83, 21.42. HRMS calcd for $C_{18}H_{15}NO_2$ 300.1000 (M + Na), found 300.1007 (M + Na).

1,4-Dimethyl-5,5-diphenylpyridine-(1*H*,5*H*)-2,6-dione (9). A 0.66 g (16.5 mmol) portion of sodium hydride (60% in mineral oil) was washed free of oil with hexane and THF and suspended in 25.0 mL of DMF, and 4.189 g (15.1 mmol) of 4-methyl-3,3-diphenylpiperidine-2,6-dione **19** was added with stirring. After the evolution of hydrogen was complete (15 min), 1.03 mL (16.5 mmol) of methyl iodide was added and the stirring continued overnight. The mixture was diluted with water, extracted with benzene, washed, dried, concentrated in vacuo, and crystallized from propanol-2 to give 3.802 g (86.4%) of 1,4-dimethyl-5,5-diphenylpyridine-(1*H*,5*H*)-2,6-dione **9**: mp 104−105 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26−7.37 (m, 10H), 6.32 (d, J = 1.5 Hz, 1H), 3.22 (s, 3H), 1.70 (d, J = 1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 175.87, 164.48, 157.00, 139.78, 129.68, 128.71, 128.25, 120.40, 64.14, 26.94, 21.48. HRMS calcd for $C_{19}H_{17}NO_2$ 314.1157 (M + Na), found 314.1147 (M + Na).

***endo*,*exo*-3-Methyl-1,6-diphenyl-3-azabicyclo[3.1.0]hexane-2,4-diones 22 and 23.** To a stirred solution of 506 mg (2.71 mmol) of 1-methyl-3-phenylmaleimide,[7] 820 mg (3.52 mmol) of dimethylbenzylsulfonium bromide, and 37 mg (0.14 mmol) of triethylbenzylammonium bromide in 10.0 mL of dichloromethane was added 2.5 mL of 50% sodium hydroxide solution at 0 °C, and the stirring continued overnight. The mixture was diluted with water, extracted with ether, washed with brine, dried over sodium sulfate, concentrated in vacuo, and chromatographed on silica gel (column

12.0 cm × 2.5 cm, eluent = hexane/ether 7:1, then 4:1) to give the following products:

Fraction 1. 2.6 mg unidentified.

Fraction 2. 56 mg (74.6%). *endo*-3-Methyl-1,6-diphenyl-3-azabicyclo[3.1.0]hexane-2,4-dione **22**: mp 126.5−127 °C (heptane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53−7.58 (m, 2H), 7.26−7.48 (m, 8H), 3.42 (d, J = 8.4 Hz, 1H), 3.15 (d, J = 8.4 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 173.86, 173.21, 132.99, 132.87, 129.27, 129.18, 129.15, 129.12, 128.67, 128.46, 42.79, 41.82, 32.43, 23.96. HRMS calcd for $C_{18}H_{15}NO_2$ 300.1000 (M + Na), found 300.1013 (M + Na).

Fraction 3. 27 mg (3.6%). *exo*-3-Methyl-1,6-diphenyl-3-azabicyclo-[3.1.0]hexane-2,4-dione **23**: mp 197.5−199 °C (heptane; lit.[7] 196−198 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.24−7.25 (m, 5H), 7.09−7.12 (m, 3H), 6.82−6.85 (m, 2H), 3.30 (d, J = 3.6 Hz, 1H), 3.12 (d, J = 3.6 Hz, 1H), 3.00 (s, 3H).

***endo,exo*-3,6-Dimethyl-1,6-diphenyl-3-azabicyclo[3.1.0]hexane-2,4-diones 28 and 29.** To a stirred solution of 159 mg (0.85 mmol) of 1-methyl-3-phenylmaleimide,[7] 390 mg (1.33 mmol) of dimethyl-(1-phenylethyl)sulfonium iodide, and 12 mg (0.044 mmol) of triethylbenzylammonium bromide in 5.0 mL of dichloromethane was added 1.0 mL of 50% sodium hydroxide solution at 0 °C, and the stirring continued overnight. The mixture was diluted with water, extracted with ether, washed with brine, dried over sodium sulfate, concentrated in vacuo, and chromatographed on silica gel (column 40.0 cm × 2.5 cm, eluent = hexane/ether 6:1) to give the following products:

Fraction 1. 11 mg (4.6%). *exo*-3,6-Dimethyl-1,6-diphenyl-3-azabicyclo[3.1.0]hexane-2,4-dione **29**: mp 174−175 °C (heptane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.24−7.29 (m, 2H), 7.02−7.18 (m, 8H), 3.47 (s, 1H), 2.99 (s, 3H), 1.61 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 174.46, 173.82, 139.75, 130.63, 129.13, 128.71, 128.49, 128.22, 127.75, 127.45, 48.98, 45.71, 34.09, 24.52, 19.90. HRMS calcd for $C_{19}H_{17}NO_2$ 314.1157 (M + Na), found 314.1165 (M + Na).

Fraction 2. 192 mg (77.8%). *endo*-3,6-Dimethyl-1,6-diphenyl-3-azabicyclo[3.1.0]hexane-2,4-dione **28**: mp 134−135 °C (heptane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55−7.58 (m, 2H), 7.27−7.50 (m, 8H), 3.00 (s, 1H), 2.33 (s, 3H), 1.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 174.39, 173.84, 138.98, 130.45, 130.33, 129.24, 129.00, 128.68, 128.40, 128.14, 48.65, 48.84, 36.74, 25.45, 23.95. HRMS calcd for $C_{19}H_{17}NO_2$ 314.1157 (M + Na), found 314.1156 (M + Na).

1,3-Dimethyl-6,6-diphenyl-3-azabicyclo[3.1.0]hexane-2,4-dione 27. A solution of 1.065 g (5.43 mmol) of diphenyldiazomethane in 10.0 mL of benzene was added to a refluxed solution of 453 mg (3.62 mmol) of 1,3-dimethylmaleimide in 10 mL of benzene during 3 h by a syringe pump. The mixture was refluxed for 12 h, cooled, concentrated in vacuo, and chromatographed on silica gel (column 12.0 cm × 2.5 cm, eluent = hexane/ether 4:1) to give 897 mg (85.1%) of 1,3-dimethyl-6,6-diphenyl-3-azabicyclo[3.1.0]hexane-2,4-dione **27**: mp 116.5−118 °C (propanol-2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.15−7.38 (m, 10H), 3.10 (s, 1H), 2.33 (s, 3H), 1.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 177.03, 174.11, 138.90, 138.75, 129.19, 129.11, 128.90, 128.65, 127.98, 127.89, 54.26, 37.32, 35.81, 23.88, 11.73. HRMS calcd for $C_{19}H_{17}NO_2$ 605.2416 (2M + Na), found 605.2423 (2M + Na) (most intense peak, monomer peak weaker).

Irradiation of 1-Methyl-3,3-diphenylpyridine-2,6-(1*H*,3*H*)-dione in Methanol. A solution of 400 mg (1.44 mmol) of 1-methyl-3,3-diphenylpyridine-2,6-(1*H*,3*H*)-dione in 250 mL of methanol was purged with nitrogen for 1 h. The irradiation was then carried out with the 0.2 M $CuSO_4$ filter solution for 6 h. TLC indicated two new distinctive spots. The solution was concentrated in vacuo and separated by chromatography (column 12.0 cm × 2.5 cm, eluent = hexane/ether 4:1) to give the following products:

Fraction 1. 201 mg. Reactant.

Fraction 2. 73.4 mg (36.9%). [2 + 2] Adduct **30**; mp 126−127.5 °C (heptane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.54−7.57 (m, 4H), 7.30−7.47 (m, 16H), 3.41 (d, J = 8.7 Hz, 2H), 3.15 (d, J = 8.4 Hz, 2H), 2.44 (s, 6H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 173.46, 172.81, 132.52, 132.42, 128.84, 128.75, 128.71, 128.28, 128.04, 42.36, 41.39, 31.98, 23.55. HRMS calcd for $C_{36}H_{30}N_2O_4$ 577.2103 (M + Na), found 577.2130 (M + Na).

Fraction 3. 44.3 mg (22.3%). 3-Methyl-6,6-diphenyl-3-azabicyclo-[3.1.0]hexane-2,4-dione **31**: mp 156−157 °C (propanol-2; lit.[9] 157 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39−7.43 (m, 2H), 7.20−7.34 (m, 8H), 3.17 (s, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 173.34, 141.40, 136.40, 129.54, 129.31, 129.11, 128.45, 127.94, 127.14, 50, 46, 34.11, 23.89. HRMS calcd for $C_{18}H_{15}NO_2$ 300.1000 (M + Na), found 300.1002 (M + Na).

Fraction 4. 15.3 mg (7.7%). Unidentified.

Irradiation of 1,3-Dimethyl-5,5-diphenylpyridine-(1*H*,5*H*)-2,6-dione (8) in Benzene. A solution of 400 mg (1.37 mmol) of 1,3-dimethyl-5,5-diphenylpyridine-(1*H*,5*H*)-2,6-dione **8** in 250 mL of benzene was purged with nitrogen for 1 h. The irradiation was then carried out with the 0.2 M $CuSO_4$ filter solution for 1 h. TLC indicated one new spot. The irradiation was continued for 3 more hours, achieving practically complete conversion of the starting material. The solution was concentrated in vacuo and crystallized from propanol-2 to give 320 mg (80%) of 1,3-dimethyl-5,6-diphenyl-3-azabicyclo[3.1.0]hexane-2,4-dione **25**: mp 130−131 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26−7.49 (m, 10H), 3.33 (s, 1H), 2.45 (s, 3H), 1.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 175.91, 174.78, 133.65, 131.68, 130.49, 129.23, 129.08, 129.06, 128.87, 128.29, 46.06, 45.86, 38.11, 24.02, 12.09. HRMS calcd for $C_{19}H_{17}NO_2$ 314.1157 (M + Na), found 314.1172 (M + Na).

Irradiation of 1,3-Dimethyl-5,5-diphenylpyridine-(1*H*,5*H*)-2,6-dione 8 in Methanol. A solution of 300 mg (1.03 mmol) of 1,3-dimethyl-5,5-diphenylpyridine-(1*H*,5*H*)-2,6-dione **8** in 250 mL of methanol was purged with nitrogen for 1 h. The irradiation was then carried out with the 0.2 M $CuSO_4$ filter solution for 6 h. TLC indicated two new distinctive spots. The solution was concentrated in vacuo and separated by chromatography (column 12.0 cm × 2.5 cm, eluent = hexane/ether 4:1) to give the following products:

Fraction 1. 13.1 mg. Starting material.

Fraction 2. 155.3 mg (54.1%). 1,3-Dimethyl-5,6-diphenyl-3-azabicyclo[3.1.0]hexane-2,4-dione **25**.

Fraction 3. 77.5 mg (27.0%). 1,3-Dimethyl-6,6-diphenyl-3-azabicyclo[3.1.0]hexane-2,4-dione **27**.

Irradiation of 1,4-Dimethyl-5,5-diphenylpyridine-(1*H*,5*H*)-2,6-dione 9 in Benzene. A solution of 200 mg (0.69 mmol) of 1,4-dimethyl-3,3-diphenylpyridione-(1*H*,3*H*)-2,6 in 250 mL of benzene was purged with nitrogen for 1 h. The irradiation was then carried out with the 0.2 M $CuSO_4$ filter solution for 2 h. TLC indicated 2 new spots and practically complete conversion of the starting material. The mixture was separated by chromatography (column 40.0 cm × 2.5 cm, eluent hexane-ether 6:1) to give the following products:

Fraction 1. 52.2 mg (26.1%). *exo*-3,6-Dimethyl-1,6-diphenyl-3-azabicyclo[3.1.0]hexane-2,4-dione **29**.

Fraction 2. 133.5 mg (66.8%). *endo*-3,6-Dimethyl-1,6-diphenyl-3-azabicyclo[3.1.0]hexane-2,4-dione **28**.

Irradiation of 1,4-Dimethyl-5,5-diphenylpyridine-(1*H*,5*H*)-2,6-dione (9) in Methanol. A solution of 200 mg (0.69 mmol) of 1,4-dimethyl-3,3-diphenylpyridione-(1*H*,3*H*)-2,6 in 250 mL of methanol was purged with nitrogen for 1 h. The irradiation was then carried out with the 0.2 M $CuSO_4$ filter solution for 1 h. TLC indicated three new spots. The solution was concentrated in vacuo and separated by chromatography (column 40.0 cm × 2.5 cm, eluent = hexane/ether 6:1) to give the following products:

Fraction 2. 50.3 mg. Starting material.

Fraction 2. 27.2 mg (18.2%). *exo*-3,6-Dimethyl-1,6-diphenyl-3-azabicyclo[3.1.0]hexane-2,4-dione **29**.

Fraction 3. 53.7 mg (35.9%). *endo*-3,6-Dimethyl-1,6-diphenyl-3-az-bicyclo[3.1.0]hexane-2,4-dione **28**.

Fraction 3. 46.8 mg (31.3%). 1,3-Dimethyl-6,6-diphenyl-3-azabicyclo[3.1.0]hexane-2,4-dione **27**.

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Supporting Information Available: Experimental procedures, NMR spectra, X-ray data, and computational files. This material is available free of charge via the Internet http://pubs.acs.org.

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