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# Solid-State Photodimerization of 2-Phenylethenyl Enamides

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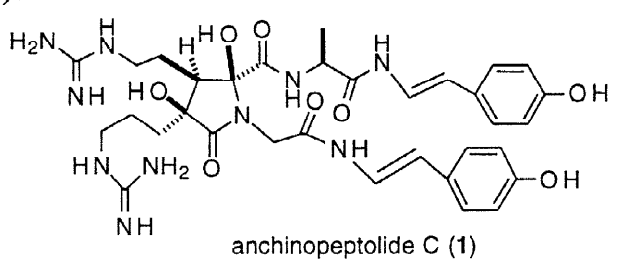
**Abstract**

Enamides **3a-c** and **6** crystallize in α-packing modes with short intermolecular distances of 3.7-4.0 Å between alkene carbon atoms of adjacent molecules related by a center of symmetry. Irradiation at 350 nm of these crystalline tertiary phenylethenyl enamides affords head-to-tail dimers **8a-c** and **9**, respectively, in 87-92% yield, in marked contrast to the *E* to *Z* isomerization that is the exclusive reaction upon solution irradiation of enamides **3a** and **6**. 

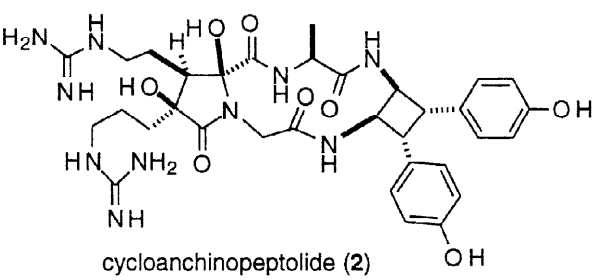
*Keywords:* cyclobutanes; dimerization; enamides; photochemistry

## Introduction

Minale and coworkers recently reported the isolation of a series of dimeric peptide alkaloids from the mediterranean sponge *Anchinoe tenacior*.[1] The structure of cycloanchinopeptolide (**2**) is particularly intriguing since it contains a cyclobutane ring that is formally derived from a [2 + 2] head-to-head cycloaddition of the two enamides of anchinopeptolide C (**1**).



anchinopeptolide C (**1**)



cycloanchinopeptolide (**2**)

To the best of our knowledge, there are no examples of either thermal or photochemical [2 + 2] cycloadditions of acyclic enamides despite the fact that the photochemistry of these systems has been extensively investigated.[2] For instance, Hoffmann and Eicken found that irradiation of tertiary trans enamides **3a** and **6** in cyclohexane with filtered light (>300 nm) results in clean isomerization to the cis enamides **4** and **7**, while irradiation of **6** with unfiltered light (254 nm) leads to a 1,3-acyl shift to give **5**, which reacts further.[3]

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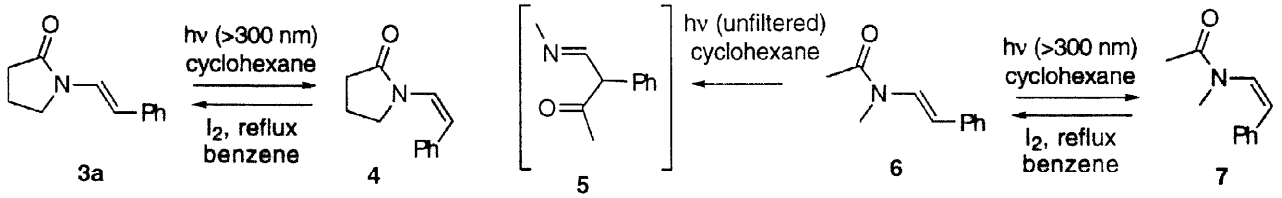



The solid-state photodimerization of crystalline *trans*-cinnamic acids, studied in the 1960's by Schmidt,[4] provides an excellent example of the *topochemical postulate*, which states that reaction in the solid state occurs with a minimum amount of atomic or molecular movement.[4] The regiochemistry of these cinnamic acid cycloadditions is controlled by crystal packing, *viz.*, depending upon the arrangement of *pairs* of reactants in the crystalline state, either head-to-head or head-to-tail dimers may be formed.[5] Reactive crystals contain molecules with parallel alkene moieties at distances ≤ 4.2 Å.[5-8]

Examination of the published structure of **3a**, reported in 1992,[9] suggests that the enamides pack in an appropriate centrosymmetric orientation (α-packing) to undergo head-to-tail dimerization upon irradiation if the intermolecular distances are ≤ 4.2 Å. We obtained the atomic coordinates and unit cell information from the Cambridge Structural Database,[10] and found a short intermolecular distance of 3.951 Å between alkene carbon atoms of adjacent molecules related by a center of symmetry (Figure 1). This arrangement is well within the criteria established by Schmidt;[5] we therefore began an investigation of the solid-state photochemistry of crystalline **3a**.

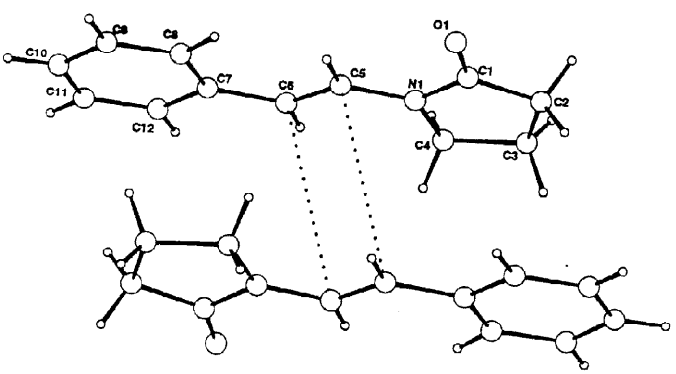



**Figure 1.** Two molecules of **3a**, showing intermolecular distances of 3.951 Å between alkene carbon atoms (dotted lines).[9]

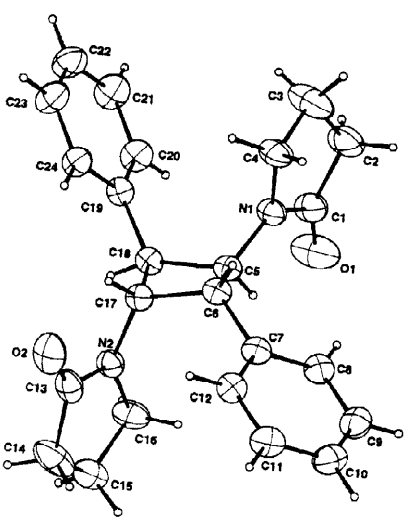
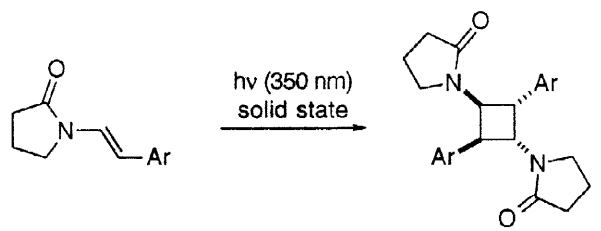


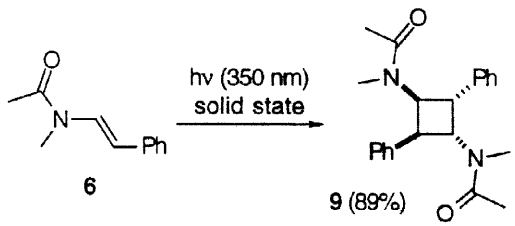

**Figure 2.** Molecular structure of dimer **8a**; 35% probability ellipsoids are shown in this and all subsequent Figures.

We were delighted to find that irradiation of crystalline **3a**[3,11] at 350 nm for 23 h gives the expected cyclobutane **8a** in 87% yield after chromatographic purification. Analysis of $^1$H NMR spectra of aliquots indicates that <3% of the *Z* isomer **4** is formed and slowly disappears on extended irradiation so that only dimer **8a** is present after extended irradiation. Crystals of the *Z* isomer **4**[3] do not react on irradiation.




**3a**, Ar = Ph
**3b**, Ar= 2-chlorophenyl
**3c**, Ar = 3-chlorophenyl

**8a**, Ar = Ph (87%)
**8b**, Ar= 2-chlorophenyl (92%)
**8c**, Ar = 3-chlorophenyl (90%)




**6**

**9** (89%)

The head-to-tail structure of dimer **8a** was established by an X-ray structure determination (Figure 2). The molecule is slightly puckered and does not have crystallographically-imposed $C_i$ symmetry; the absolute values of the torsion angles of the cyclobutane moiety range from 10.1 to 10.3°. These torsion angles and those of other dimers reported below lie well within the ranges reported for cyclobutane rings.[12]

Introduction of chlorine substituents onto the aromatic ring of planar aromatic compounds often leads to β-packing modes with head-to-head stacking and a short repeat distance of ≈ 4 Å.[13] Thus 2- and 3-chlorocinnamic acids have unit cells containing short axes (*ca.* 3.9 Å)[5,14] and form *head-to-head* dimers upon solid-state irradiation. In an attempt to prepare

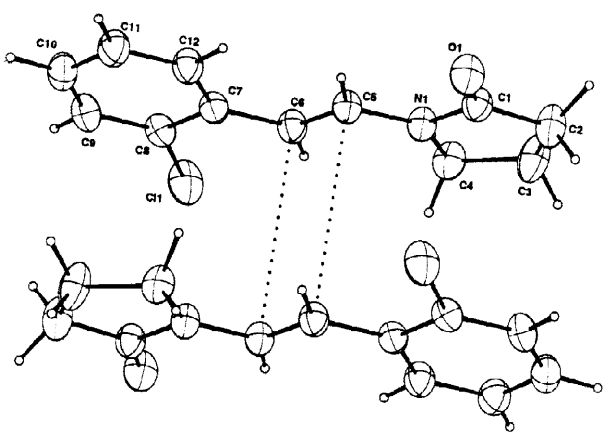



**Figure 3.** Pairs of molecules of **3b** showing intermolecular distances of 3.918 Å.

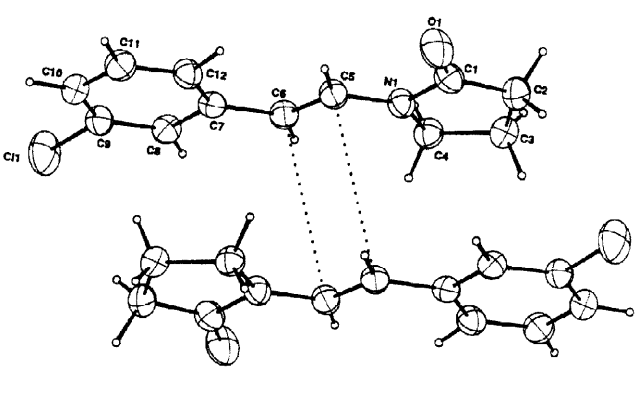



**Figure 4.** Pairs of molecules of **3c** showing intermolecular distances of 3.904 Å.

head-to-head dimers analogous to **2**, we prepared **3b** and **3c** by condensation of the appropriate chlorophenylacetaldehyde with 2-pyrrolidinone.[11] However, X-ray structure determinations of **3b** and **3c** reveals head-to-tail arrangements of pairs of reactant molecules (α-packing) similar to that of **3a**, with intermolecular distances of 3.918 and 3.904 Å, respectively, between alkene carbon atoms of adjacent molecules related by a center of symmetry (Figures 3 and 4). As expected, irradiation of crystalline **3b** and **3c** at 350 nm for 15-20 h provides 90% of cyclobutanes **8b** and **8c** resulting from head-to-tail dimerization. The molecular structures of **8b** and **8c** shown in Figures 5 and 6 indicate that the cyclobutane rings are slightly puckered and do not have crystallographically-imposed $C_i$ symmetry; the absolute values of the torsion angles of the cyclobutane moiety range from 11.7 to 11.9° in **8b** and from 17.1 to 17.5° in **8c**.

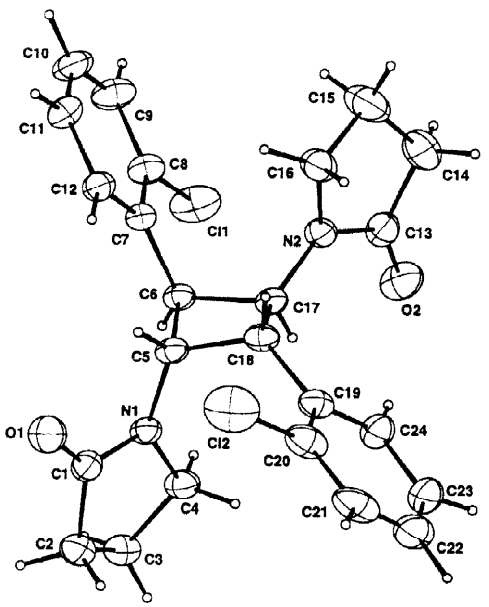



**Figure 5.** Molecular structure of dimer **8b**.

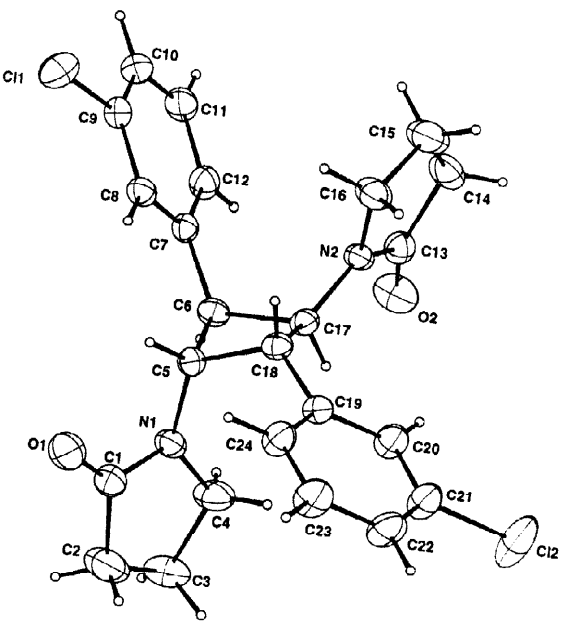



**Figure 6.** Molecular structure of dimer **8c**.

Solid-state photodimerization of enamides is not restricted to those derived from pyrrolidinone. An X-ray structure determination of **6** indicates that it also packs in a head-to-tail orientation with intermolecular distances of 3.718 Å (Figure 7). Irradiation of crystalline **6** at 350 nm for 21 h affords 89% of **9**, which has crystallographically-imposed $C_i$ symmetry and a planar cyclobutane ring (Figure 8).

Secondary enamide **10**[15] was prepared by decarboxylation of *N*-acetylamidocinnamic acid.[15a] Although **10** is crystalline, we were unable to obtain suitable crystals for structure determination. Irradiation of crystalline **10** leads only to isomerization to the *Z* isomer **11** in 43% yield.

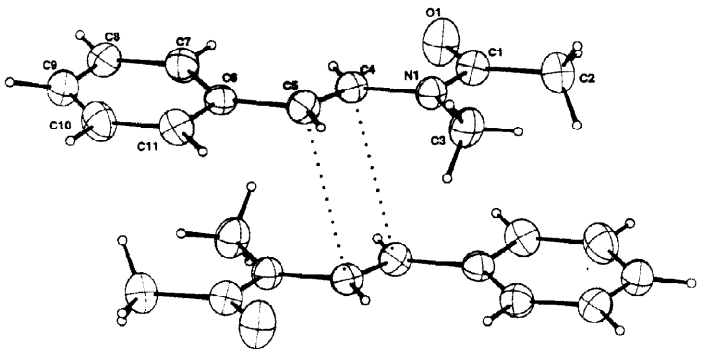


**Figure 7.** Two molecules of **6**, showing intermolecular distances of 3.718 Å between alkene carbon atoms.

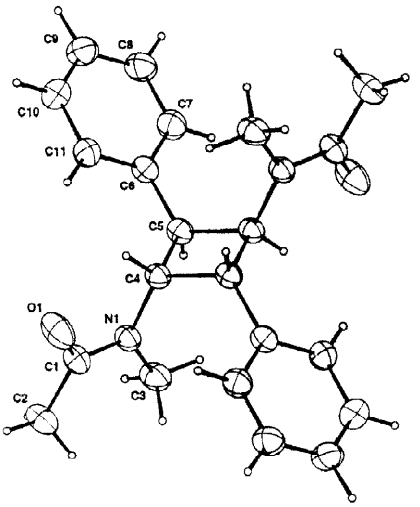
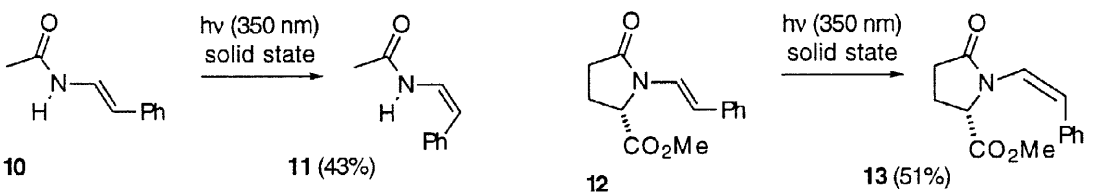


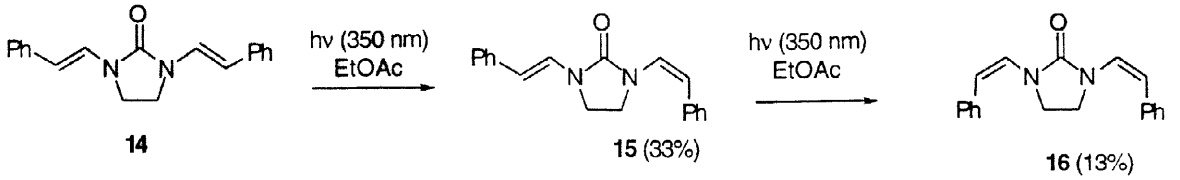
**Figure 8.** Molecular structure of dimer **9**.

Tertiary enamide **12** was prepared from methyl pyroglutamate[16] since the presence of the ester group should preclude packing in the orientation observed with **3a**. An X-ray structure determination of **12** showed that there are no contacts between alkene carbon atoms shorter than 5.1 Å. Figure 9 shows the closest approach of two nearly parallel molecules (interplanar angle 4.9°). However, the shortest contact between alkene carbon atoms of adjacent molecules is 5.848 Å. As expected, irradiation of crystalline **12** provides 51% of the *Z* isomer **13** and no cyclobutane.




**10** **11** (43%) **12** **13** (51%)

Bis enamide **14** was prepared by condensation of imidazolidinone with phenylacetaldehyde. X-ray structure determination of **14** reveals contacts between alkene carbon atoms of adjacent molecules as short as 4.402 Å, approximately 0.2 Å longer than the 4.2 Å criterion which applies to most [2 + 2] photocycloadditions.[4-8] However, these contacts are between *nearly orthogonal* molecules (interplanar angle 101.5°) as shown in Figure 10. No reaction occurs on irradiation of crystalline **14**. Irradiation in EtOAc solution leads to the *E, Z* isomer **15** and then the *Z, Z* isomer **16** in yields that depend on the time of irradiation. After 12 h, we obtained 13% of **16**, 33% of **15** and 13% of recovered **14**.




14 15 (33%) 16 (13%)

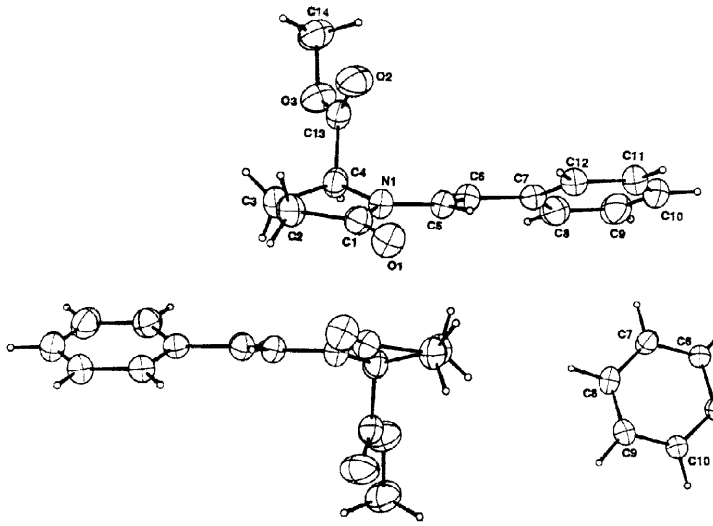


**Figure 9.** Two nearly parallel molecules of **12**. The distance between the nearest pair of alkene carbon atoms is 5.848 Å.

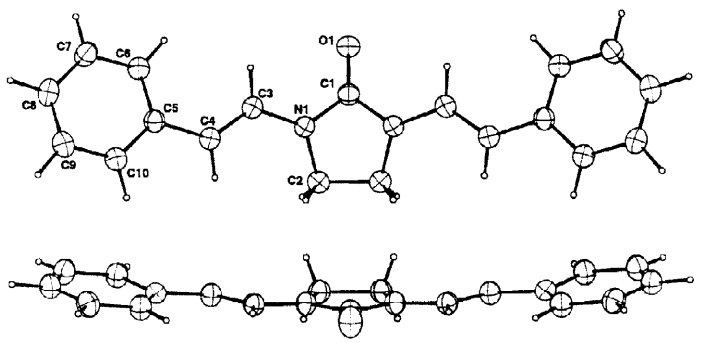
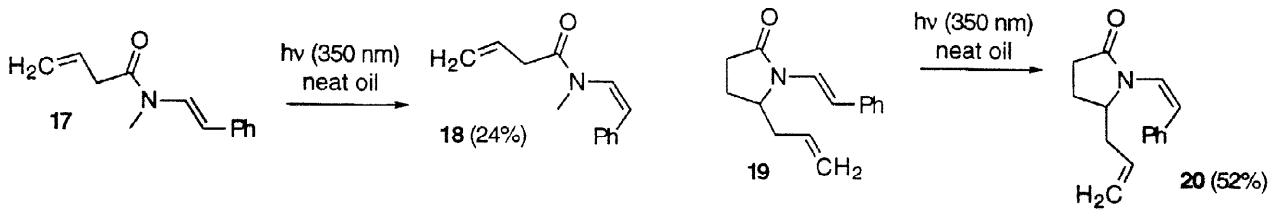


**Figure 10.** Two nearly orthogonal molecules of **14**. The distance between the nearest pair of alkene carbon atoms is 4.402 Å.

The successful solid-state photodimerizations of **3a**, **3b**, **3c**, and **6** indicate that addition of the excited state of the enamide to an adjacent double bond in the crystal can be faster than *E* to *Z* isomerization of the double bond if the two double bonds are in close proximity. We therefore were interested to determine whether intramolecular [2 + 2] cycloadditions of unsaturated enamides could compete with *E* to *Z* isomerization, as may be occurring in the biosynthesis of cycloanchinopeptolide (**2**) from anchinopeptolide C (**1**). We therefore prepared **17** from *N*-methyl-3-butenamide and **19** from 5-allyl-2-pyrrolidinone. Neither of these compounds is crystalline. Irradiation of **17** and **19** as neat oils at 350 nm for 2 d leads only to *E* to *Z* isomerization of the enamides giving **18** (24%) and **20** (52%). Similar results are obtained in dilute EtOAc solution. Therefore *E* to *Z* isomerization of the double bond is faster than intramolecular [2 + 2] cycloaddition to the terminal double bond in these cases.




In conclusion, we have established that facile head-to-tail photodimerization of tertiary phenylethenyl enamides occurs in the solid state, in marked contrast to the *E* to *Z* isomerization that is the exclusive reaction in solution.

## Experimental Section

**General Procedures.** NMR spectra were recorded at 300 MHz in $CDCl_3$. Chemical shifts are reported in δ (ppm) and coupling constants in Hz. IR spectra are reported in $cm^{-1}$. 2- and 3-Chlorophenylacetaldehyde were prepared by Darzens glycidic ester condensation on 2- and 3-chlorobenzaldehyde, followed by hydrolysis and decarboxylation of the glycidic ester.[17] 5-Allylpyrrolidinone was prepared by reaction of 5-methoxypyrrolidinone[18] with allyl bromide and Zn.[19]

**General Procedure for Preparation of Tertiary Enamides.** A solution of 10 mmol of the appropriate lactam or amide, 10 mmol of the desired aldehyde, and 5 mg of *p*-toluenesulfonic acid in 15-20 mL of dry toluene was heated at reflux with water removal by a Dean-Stark trap for 10-24 h until no more water was collected. The solution was then cooled to 25 °C, and washed with 10 mL of saturated sodium bicarbonate solution and 10 mL of water. The combined aqueous layers were extracted with 10 mL of ether. The organic phases were combined and dried ($MgSO_4$), filtered, and concentrated. The residue was then either recrystallized from ethyl acetate or purified by flash chromatography on silica gel.

***N*-(*E*-2-Phenylethenyl)-2-pyrrolidinone (3a)**: 75% yield; mp 126.5-127.5 °C; $^1$H NMR 7.61 (d, 1, *J* = 14.9), 7.15-7.35 (m, 5), 5.85 (d, 1, *J* = 14.9), 3.58 (t, 2, *J* = 7.2), 2.49 (t, 2, *J* = 7.8), 1.95-2.15 (m, 2); $^{13}$C NMR 173.1, 136.2, 128.4, 126.3, 125.4, 123.3, 111.5, 45.0, 31.0, 17.2; IR (KBr) 1696, 1649, 1480, 1452, 1405, 1340, 1288, 1241, 960, 752, 698.

***N*-[*E*-2-(2-Chlorophenylethenyl)]-2-pyrrolidinone (3b)**: 80% yield; mp 138.5-139 °C; $^1$H NMR 7.60 (d, 1, *J* = 14.8), 7.10-7.55 (m, 4), 6.21 (d, 1, *J* = 14.8), 3.69 (t, 2, *J* = 7.1), 2.55 (t, 2, *J* = 7.8), 2.10-2.23 (m, 2); $^{13}$C NMR 173.5, 134.4, 132.3, 129.5, 127.4, 126.9, 125.6, 125.3, 107.7, 45.2, 31.3, 17.3; IR (KBr) 1687, 1419, 1288, 766.

***N*-[*E*-2-(3-Chlorophenylethenyl)]-2-pyrrolidinone (3c)**: 75% yield; mp 106.0-107.5 °C; $^1$H NMR 7.61 (d, 1, *J* = 14.9), 7.10-7.38 (m, 4), 5.79 (d, 1, *J* = 14.9), 3.62 (t, 2, *J* = 7.3), 2.54 (t, 2, *J* = 7.5), 2.16 (m, 2); $^{13}$C NMR 173.4, 138.3, 134.5, 129.8, 126.3, 125.5, 124.6, 123.5, 110.1, 45.1, 31.1, 17.4; IR (KBr) 1696, 1651, 1428, 1398, 1348, 1321, 1245, 1100, 957, 779, 688.

***N*-Methyl-*N*-(*E*-2-phenylethenyl)acetamide (6)**: 80% yield; 2.3:1 mixture of rotamers; mp 81-81.5 °C; $^1$H NMR 8.09 (d, 0.3 × 1, *J* = 14.9), 7.10-7.39 (m, 5 + 0.7 × 1), 5.96 (d, 0.7 × 1, *J* = 14.9), 5.92 (d, 0.3 × 1, *J* = 14.9), 3.20 (s, 3), 2.31 (s, 0.7 × 3), 2.25 (s, 0.3 × 3); $^{13}$C NMR (major rotamer) 169.3, 136.4, 128.9, 128.7, 126.5, 125.3, 111.0, 29.4, 21.9; (minor rotamer) 169.1, 136.7, 128.5, 127.1, 126.3, 125.6, 110.7, 33.0, 22.7; IR (KBr) 1637, 1445, 1388, 1310, 1261, 1143, 1014, 960, 753, 693.

**Methyl 5-Oxo-*N*-(*E*-2-phenylethenyl)pyrrolidine-2-carboxylate (12)**: silica gel (3:2:2 hexane/EtOAc/$CH_2Cl_2$); 45% yield; mp 109-111 °C; $^1$H NMR 7.58 (d, 1, *J* = 15.0), 7.13-7.38 (m, 5), 5.80 (d, 1, *J* = 15.0), 4.57 (dd, 1, *J* = 1.9, 9.2), 3.79 (s, 3), 2.15-2.80 (m, 4); $^{13}$C NMR 173.2, 171.7, 135.9, 128.6, 126.8, 125.7, 122.7, 112.0, 58.3, 52.8, 29.8, 23.0; IR (KBr) 1743, 1682, 1648, 1627, 1596, 1450, 1408, 1296, 1239, 1210, 989, 954, 757, 698.

**1,3-Di-(*E*-phenylethenyl)-2-imidazolidinone (14)**: 40% yield; mp 205-206 °C; $^1$H NMR 7.58 (d, 2, $J$ = 14.6), 7.10-7.40 (m, 10), 5.70 (d, 2, $J$ = 14.6), 3.80 (s, 4); $^{13}$C NMR 136.5, 128.7, 126.1, 125.2, 124.3, 108.5, 40.0 (the carbonyl carbon was not observed); IR (KBr) 1702, 1647, 1492, 1430, 1303, 1252, 1155, 943, 744, 691.

***N*-Methyl-*N*-(*E*-2-phenylethenyl)-3-butenamide (17)**: silica gel (8:1:1 hexane/MeOH/EtOAc); 10% yield; 3:2 mixture of rotamers; $^1$H NMR 8.10 (d, 0.4 × 1, $J$ = 14.9), 7.13-7.38 (m, 5.6), 5.78-6.11 (m, 2), 5.11-5.28 (m, 2), 3.37 (m, 0.6 × 2), 3.29 (m, 0.4 × 2), 3.21 (s, 0.6 × 3), 3.19 (s, 0.4 × 3); $^{13}$C NMR (major rotamer) 169.7, 136.4, 130.7, 128.6, 128.3, 126.4, 125.3, 118.3, 111.3, 39.1, 29.6; (minor rotamer) 169.4, 136.6, 130.6, 128.5, 127.2, 126.3, 125.6, 118.2, 110.9, 39.5, 32.3; IR (neat) 1672, 1633, 1599, 1470, 1416, 1385, 1328, 1237, 1095, 925, 750, 694.

***N*-(*E*-2-Phenylethenyl)-5-(2-propenyl)-2-pyrrolidinone (19)**: silica gel (4:1 hexane/EtOAc); 67% yield; $^1$H NMR 7.53 (d, 1, $J$ = 15.2), 7.13-7.40 (m, 5), 5.95 (d, 1, $J$ = 15.2), 5.68-5.85 (m, 1), 5.15 (m, 2), 4.14 (m, 1), 1.90-2.72 (m, 6); $^{13}$C NMR 173.2, 136.3, 132.5, 128.5, 126.4, 125.4, 122.2, 118.9, 112.2, 58.8, 35.4, 29.9, 22.6; IR (neat) 1701, 1644, 1399, 1288, 1232, 952, 752, 694.

**General Procedure for Photoirradiation.** Photochemical [2 + 2] cycloadditions and *E* to *Z* isomerizations were carried out in a cylindrical photoreactor with eighteen fluorescent, twelve-inch long, 8 Watt, 350 nm blacklights (GE F8T5-BLB).

***N*-(*Z*-2-Phenylethenyl)-2-pyrrolidinone (4).** A solution of **3a** (40 mg) in 10 mL of EtOAc in a pyrex test tube was irradiated at 350 nm for 32 h. Evaporation of the solvent and purification of the residue by flash chromatography on silica gel (8:2:1 hexane/EtOAc/MeOH) gave 34 mg (85%) of pure **4**: mp 69.5-71.0 °C; $^1$H NMR 7.16-7.37 (m, 5), 6.80 (d, 1, $J$ = 10.0), 5.99 (d, 1, $J$ = 10.0), 3.20 (t, 2, $J$ = 7.0), 2.41 (t, 2, $J$ = 8.1), 1.87-2.00 (m, 2); $^{13}$C NMR 175.5, 136.2, 129.1, 127.8, 126.8, 123.8, 113.7, 48.0, 30.3, 18.8; IR (KBr) 1696, 1649, 1409, 1380, 1338, 1268, 765, 708.

**(1α,2α,3β,4β)-1,3-Bis(1-(2-oxopyrrolidinyl))-2,4-diphenylcyclobutane (8a).** Irradiation of 58 mg of **3a** in a pyrex dish at 350 nm for 23 h resulted in quantitative conversion to **8a** as determined by analysis of the $^1$H NMR spectrum. Purification by flash chromatography on silica gel (1:1 EtOAc/$CHCl_3$) gave 51 mg (87%) of pure **8a**: mp 196.5-198 °C; $^1$H NMR 7.14-7.44 (m, 10), 5.67 (dd, 2, $J$ = 7.8, 9.3), 4.21 (dd, 2, $J$ = 7.8, 9.3), 3.20-3.44 (m, 2), 2.52-2.67 (m, 2), 2.07-2.40 (m, 4), 1.65-1.85 (m, 2), 1.40-1.58 (m, 2); $^{13}$C NMR 175.5, 137.1, 128.6, 126.9, 126.8, 50.0, 45.5, 45.1, 31.1, 18.2; IR (KBr) 1679, 1592, 1495, 1420, 1287, 759, 712.

**(1α,2α,3β,4β)-1,3-Bis(1-(2-oxopyrrolidinyl))-2,4-bis(2-chlorophenyl)cyclobutane (8b).** Irradiation of 61 mg of **3b** in a pyrex dish at 350 nm for 21 h resulted in quantitative conversion to **8b** as determined by analysis of the $^1$H NMR spectrum. Purification by chromatography on silica gel (1:1 EtOAc/$CHCl_3$) gave 56 mg (92%) of pure **8b**: mp 213-215 °C; $^1$H NMR 7.22-7.65 (m, 8), 5.91 (dd, 2, $J$ = 8.1, 9.3), 4.41 (dd, 2, $J$ = 8.1, 9.3), 3.23-3.34 (m, 2), 2.60-2.69 (m, 2), 2.21-2.29 (m, 4), 1.67-1.83 (m, 2), 1.46-1.63 (m, 2); $^{13}$C NMR 175.0, 134.7, 134.4, 129.6, 128.6, 127.6, 127.2, 48.5, 45.0, 44.8, 30.9, 18.3; IR (KBr) 1676, 1475, 1418, 1288, 1231, 1053, 763.

**(1α,2α,3β,4β)-1,3-Bis(1-(2-oxopyrrolidinyl))-2,4-bis(3-chlorophenyl)cyclobutane (8c).** Irradiation of 11 mg of **3c** in a pyrex dish at 350 nm for 15 h resulted in quantitative conversion to **8c** as determined by analysis of the $^1$H NMR spectrum. Purification by chromatography on silica gel (1:1 EtOAc/$CHCl_3$) gave 10 mg (90%) of pure **8c**: mp 195-196 °C; $^1$H NMR 7.09-7.34 (m, 8), 5.54 (dd, 2, $J$ = 7.8, 9.0), 4.16 (dd, 2, $J$ = 7.8, 9.0), 3.25-3.38 (m, 2), 2.58-2.70 (m, 2), 2.15-2.43 (m, 4), 1.75-1.91 (m, 2), 1.51-1.67 (m, 2); $^{13}$C NMR 175.7, 139.1, 134.7, 130.0, 127.2, 127.0, 125.3, 50.0, 45.3, 45.2, 31.1, 18.2; IR (KBr) 1673, 1597, 1570, 1478, 1417, 1288, 780, 688.

**(1α,2α,3β,4β)-1,3-Bis(*N*-methylacetamido)-2,4-diphenylcyclobutane (9).** Irradiation of 67 mg of **6** in a pyrex dish at 350 nm for 21 h resulted in quantitative conversion to **9** as determined by analysis of the $^1$H NMR spectrum. Purification by flash chromatography on silica gel (1:1 EtOAc/$CHCl_3$) gave 60 mg (89%) of pure **9** as a 5:1 mixture of symmetrical and unsymmetrical rotamers: mp 177-179 °C; $^1$H NMR 7.18-

7.43 (m, 10), 6.02 (dd, 0.83 × 2, $J$ = 8.2, 9.8), 5.80 (dd, 0.17 × 1, dd, $J$ = 9.0, 9.0), 5.24 (dd, 0.17 × 1, dd, $J$ = 6.5, 9.8), 4.32 (m, 0.17 × 2) 4.25 (dd, 0.83 × 2, $J$ = 8.2, 9.8), 2.68 (s, 0.17 × 3), 2.58 (s, 0.83 × 6 + 0.17 × 3), 2.22 (s, 0.17 × 3), 1.96 (s, 0.8 × 6), 1.94 (s, 0.2 × 3); $^{13}$C NMR (major rotamer) 171.4, 137.7, 128.5, 127.2, 126.6, 52.5, 45.1, 32.7, 22.3; (minor rotamer) 171.4, 171.1, 137.4, 136.9, 128.9, 128.7, 127.3, 127.1, 126.9, 126.6, 57.0, 53.9, 46.9, 46.1, 33.1, 29.9, 22.3 (2 C); IR (KBr) 1648, 1485, 1408, 1325, 1270, 1139, 1034, 1010, 747, 699, 595, 500.

***N*-(*Z*-2-Phenylethenyl)acetamide (11).** Irradiation of 27 mg of **10** in a pyrex dish at 350 nm for 18 h followed by flash chromatography on silica gel (3:2 hexane/EtOAc) gave 12 mg (43%) of **11**: mp 65-66 °C; $^1$H NMR 7.86-8.02 (br, 1, NH), 7.17-7.44 (m, 5), 6.88 (dd, 1, $J$ = 10.9, 9.8), 5.70 (d, 1, $J$ = 9.8), 2.00 (s, 3); $^{13}$C NMR 167.9, 135.4, 128.8, 127.8, 126.7, 121.8, 109.8, 23.0; IR (KBr) 3243 (br), 1651, 1516, 1368, 1270, 1091, 774, 696.

**Methyl 5-Oxo-*N*-(*Z*-2-phenylethenyl)pyrrolidine-2-carboxylate (13).** Irradiation of 75 mg of **12** in a pyrex dish at 350 nm for 63 h followed by flash chromatography on silica gel (10:2:1 $CH_2Cl_2$/hexane/EtOAc) gave 35 mg (51%) of **13**: $^1$H NMR 7.13-7.34 (m, 5), 6.73 (d, 1, $J$ = 9.7), 6.07 (d, 1, $J$ = 9.7), 4.31 (dd, 1, $J$ = 2.1, 9.2), 3.54 (s, 3), 1.93-2.52 (m, 4); $^{13}$C NMR 171.4, 135.5, 128.8, 128.1, 127.4, 123.1, 116.3, 59.2, 52.3, 28.7, 23.3 (the amide carbonyl carbon was not observed); IR (neat) 1745, 1713, 1650, 1445, 1405, 1379, 1347, 1341, 1287, 1207, 1045, 990, 765, 703.

**Irradiation of 14 in EtOAc Solution.** A solution of **14** (63 mg) in EtOAc (20 mL) was irradiated at 350 nm for 12 h. Purification by flash chromatography on silica gel (4:1 $CH_2Cl_2$/hexane) gave 8 mg (13%) of recovered **14**, followed by 20 mg (22%) of 1-(*E*-phenylethenyl)-3-(*Z*-phenylethenyl)-2-imidazolidinone (**15**), and by 8 mg (13%) of 1,3-di-(*Z*-phenylethenyl)-2-imidazolidinone (**16**).

The data for **15**: mp 152.5-154 °C; $^1$H NMR: 7.56 (d, 1, $J$ = 14.8), 7.11-7.36 (m, 10), 6.83 (d, 1, $J$ = 10.0), 5.90 (d, 1, $J$ = 10.0), 5.64 (d, 1, $J$ = 14.8), 3.55-3.63 (m, 2), 3.33-3.41 (m, 2); $^{13}$C NMR 136.6, 136.4, 129.3, 128.6, 127.8, 126.7, 126.1, 125.2, 124.6, 124.5, 110.4, 108.4, 42.7, 40.4 (the urea carbonyl carbon was not observed); IR (KBr) 1706, 1644, 1480, 1419, 1289, 1263, 749, 698.

The data for **16**: mp 104-106 °C; $^1$H NMR 7.12-7.40 (m, 10), 6.80 (d, 2, $J$ = 10.0), 5.85 (d, 2. $J$ = 10.0), 3.12 (s, 4); $^{13}$C NMR 136.4, 129.3, 127.7, 126.6, 124.7, 110.1, 43.2 (the urea carbonyl carbon was not observed); IR (KBr) 1721.4, 1654, 1482, 1445, 1413, 1267, 766, 700.

***N*-Methyl-*N*-(*Z*-2-phenylethenyl)-3-butenamide (18).** Irradiation of 129 mg of **17** in a pyrex dish at 350 nm for 60 h followed by flash chromatography on silica gel (8:2:1 $CH_2Cl_2$/hexane/EtOAc) gave 31 mg (24%) of **18**: $^1$H NMR 7.21-7.37 (m, 5), 6.41 (d, 1, $J$ = 8.8), 6.14 (d, 1, $J$ = 8.8), 5.86-6.05 (m, 1), 5.03-5.20 (m, 2), 3.17 (m, 2), 2.96 (s, 3); $^{13}$C NMR 171.0, 134.3, 131.1, 128.8, 128.6, 128.5, 128.0, 124.3, 118.0, 39.4, 34.4; IR (neat) 1667, 1633, 1447, 1402, 1367, 1265, 1176, 1077, 919, 779, 697.

***N*-(*Z*-2-Phenylethenyl)-5-(2-propenyl)-2-pyrrolidinone (20).** Irradiation of 93 mg of **19** in a pyrex dish at 350 nm for 48 h followed by flash chromatography on silica gel (10:2:1 $CH_2Cl_2$/hexane/EtOAc) gave 48 mg (52%) of **20**: $^1$H NMR 7.15-7.38 (m, 5), 6.60 (d, 1, $J$ = 9.7), 6.10 (d, 1, $J$ = 9.7), 5.20-5.37 (m, 1), 4.79-5.00 (m, 2), 3.72-3.86 (m, 1), 2.34-2.49 (m, 2), 1.72-2.12 (m, 4); $^{13}$C NMR 175.3, 136.2, 132.7, 128.8, 128.1, 127.2, 122.5, 118.6, 117.2, 56.5, 36.4, 29.3, 22.5; IR (neat) 1704, 1644, 1407, 1247, 920, 765, 700

**Structure Determination.** The authors have deposited atomic coordinates for the structures depicted in Figures 2-10 with the Cambridge Crystallographic Data Centre. The coordinates can be obtained upon request from the Director, Cambridge Crystallographic Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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