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The Intramolecular Electron Transfer Reactions of N-Alkylcyclopropyl Phthalimides

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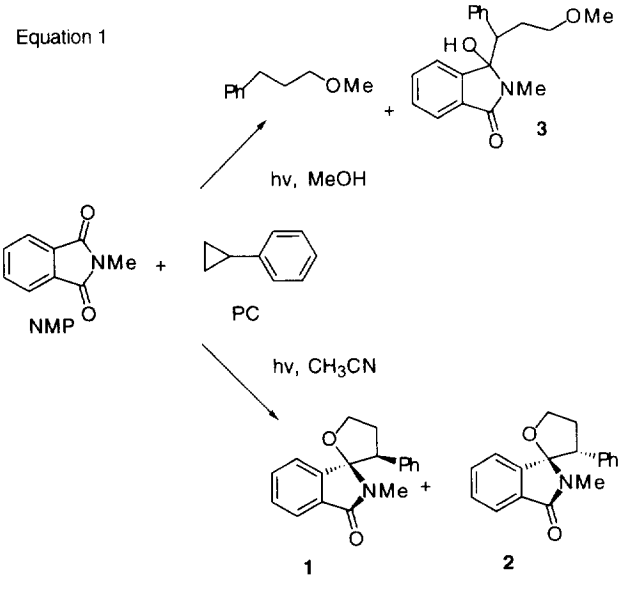
Abstract: N-Alkylcyclopropyl phthalimides **5** and **6** were photolyzed to afford spiro lactams **17**, **18** and **20-24**. These products arise via an intramolecular electron transfer reaction between the phthalimide and the phenylcyclopropane portions of the molecule. The resulting radical anion attacks the phenylcyclopropane radical cation which is followed by radical-radical coupling to afford the observed photoadducts. In addition, the isolation of olefin **19** offers additional proof that the attack of the radical anion onto the radical cation is a stepwise process rather than a concerted one.

Introduction

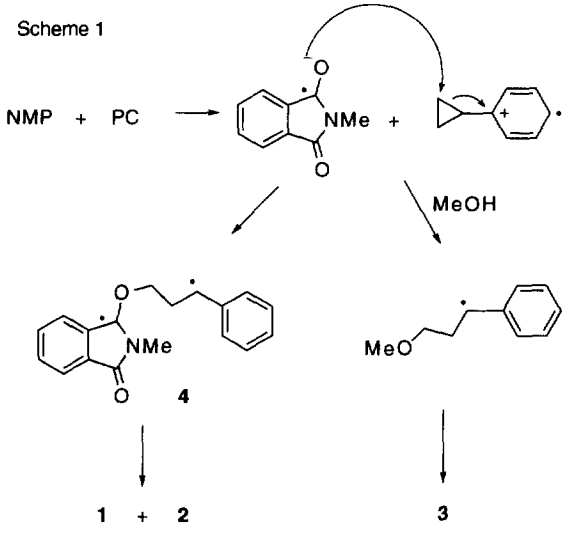
We have previously reported that N-methylphthalimide (NMP) undergoes a photolysis reaction with phenylcyclopropane (PC) in acetonitrile to afford two isomeric spiro tetrahydrofuranyl lactams **1** and **2**.[2a] When the reaction is performed in the nucleophilic solvent methanol, hydroxylactam **3** and 1-methoxy-3-phenylpropane are produced (Eq. 1).[2b]

Equation 1



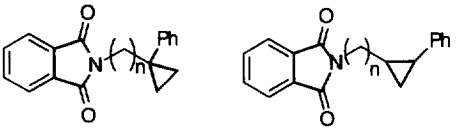
The mechanism for the formation of photoadducts **1** and **2** involves photostimulated electron transfer followed by nucleophilic attack on the phenylcyclopropane radical cation by the imide radical anion (Scheme 1). Radical-radical coupling of intermediate **4** affords lactams **1** and **2**. Alternatively in the presence of methanol, the phenylcyclopropane radical cation can undergo nucleophilic attack by methanol to afford the 1-methoxy-3-phenylpropane radical. Radical coupling with NMP radical anion and proton transfer occurs to produce hydroxylactam **3**. Fluorescence quenching studies of N-methyl-2,3-naphthalimide with various aromatic substituted phenylcyclopropanes established that the reaction proceeds *via* electron transfer.[2c] Deuterium labeling studies utilizing *cis* 2-deuterophenylcyclopropane have shown that this nucleophilic attack is a two-step process involving the intermediate biradical **4**, rather than a concerted process.[2c] The formation of spiro lactams **1** and **2** represents one of the first examples of a photochemically generated radical anion-radical cation pair undergoing cycloaddition, since most radical ion pairs undergo either rearrangement or proton abstraction prior to coupling.

Scheme 1



We investigated the generality of this reaction by extending it to the intramolecular cases utilizing the 1,1- and 1,2-substituted phenylcyclopropanes **5a,b** and **6a,b** (Figure 1). For cases where n=2 (**5b** and **6b**), attack of the imide radical anion onto the phenylcyclopropyl radical cation should occur so as to form a 6-membered ring in the photoadduct, whereas when n=1 (**5a** and **6a**), attack can occur to afford either a 5 or 6-membered ring (*vide infra*).

Figure 1



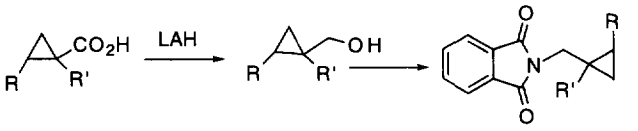
5a, n=1
5b, n=2

6a, n=1
6b, n=2

Results and Discussion

The necessary phthalimides **5** and **6** were prepared according to Schemes 2-4. The imides **5a** and **6a** were readily synthesized in two steps from commercially available 1-phenylcyclopropanecarboxylic acid **(7)** and 2-phenylcyclopropanecarboxylic acid **(9)**, respectively (Scheme 2). The appropriate acid was reduced[3] with lithium aluminum hydride (LAH) to the alcohol **8** or **10**. Mitsunobu reaction[4] of alcohol **8** or **10** with phthalimide affords the desired photosubstrates **5a** and **6a,** respectively, in good yields.

Scheme 2



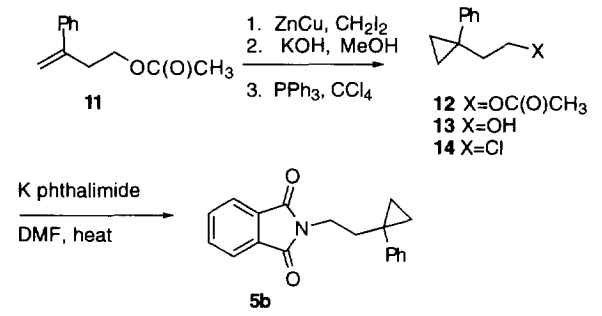
7 R=H, R'=Ph
9 R=Ph, R'=H

8 R=H, R'=Ph
10 R=Ph, R'=H

5a R=H, R'=Ph
6a R=Ph, R'=H

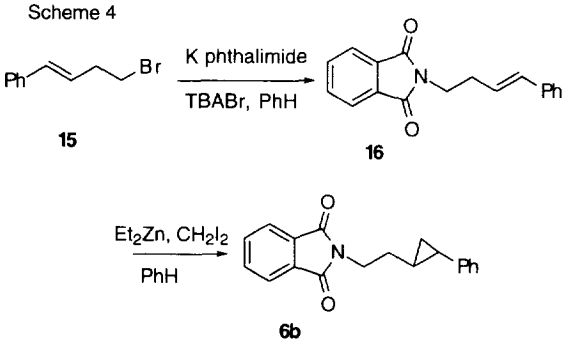
The syntheses of phthalimides **5b** and **6b** were not as straightforward. For both compounds, the cyclopropyl ring was incorporated onto the alkyl chain at some point in the synthetic sequence. 3-Phenylbut-3-ene-1-yl acetate **(11)** (Scheme 3), prepared according to literature procedure[5] from α-methyl styrene and paraformaldehyde, was reacted with freshly prepared zinc-copper couple and methylene iodide in refluxing ether to afford 2-(1-phenylcyclopropyl)ethyl acetate **(12)**[6]. Saponification of the ester gave 2-(1-phenylcyclopropyl)ethanol **(13)**[6] in 51% yield from olefin **11**. After conversion to chloride **14**, alkylation with potassium phthalimide afforded photosubstrate **5b**.

Scheme 3



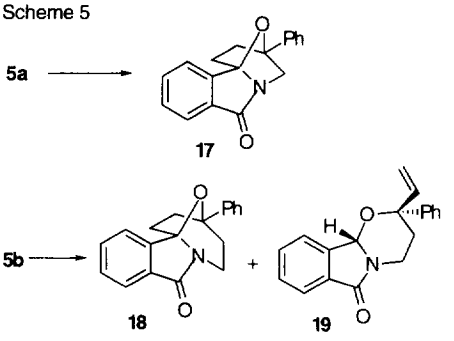
Phthalimide **16** (Scheme 4), obtained in 90% yield by alkylation of potassium phthalimide with bromoolefin **15**[7], underwent a cyclopropanation reaction with diethyl zinc and methylene iodide in refluxing benzene to give a mixture of starting olefin **16** and product **6b**. Since these two compounds were inseparable by employing standard chromatographic techniques, the crude mixture was subjected to ozonolysis. Pure desired product **6b** was obtained upon chromatography (21% yield).

Scheme 4



A nitrogen-purged solution of phthalimide **5a** in benzene was irradiated with a Pyrex filter for 5 hours (Scheme 5) to afford lactam **17** as the only product of the reaction (7% yield, 42% yield based on recovered starting material). The IR spectrum of **17** showed one carbonyl signal (1700 cm^{-1}) for the lactam. The proton NMR spectrum of **17** exhibited a 1H doublet (J=9.4 Hz) at δ 3.62 and a 1H doublet of doublets (J=2.4, 9.4 Hz) at δ 3.55 corresponding to the diastereotopic methylene group adjacent to the lactam nitrogen. In addition, a 4H multiplet at δ 2.30-2.59 for the tetrahydrofuranyl ethyl group and nine aromatic hydrogens were observed.

Scheme 5

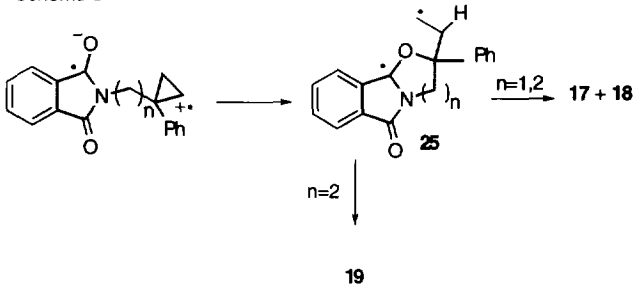


Irradiation of phthalimide **5b** (Scheme 5) afforded two products, the spirolactam **18** (61% yield) and tricyclic ether **19** (7% yield) as a single diastereomer. For lactam **18**, in addition to the signals for nine aromatic protons, the proton NMR exhibited two 1H multiplets (ddd) at δ 3.50 and 4.41 both of which are coupled to each other as well as to a 2H multiplet at δ 1.88-2.05 thus indicating that they are the diastereotopic methylene protons adjacent to the lactam. COSY experiments showed that the 2H multiplet at δ 2.55-2.70 was coupled to both of the 1H multiplets at δ 2.25-2.33 and 2.35-2.50 thus assigning the tetrahydrofuranyl ethyl group. The lactam carbonyl was observed in the IR at 1693 cm^{-1}.

The structure of the minor photoproduct **19** was elucidated by careful examination of the proton, carbon and COSY NMR experiments. The proton NMR spectrum exhibited eight 1H multiplets between δ 1.8 and 6.2. A COSY experiment established that three multiplets in the region of ~5.5 to 6.2 ppm are coupled only among themselves thus indicating the presence of a terminal olefin. In addition, each of the four upfield multiplets are coupled with each other suggesting two adjacent diastereotopic methylenes. The DEPT experiment showed two aliphatic methylene carbons, one terminal vinyl carbon, one downfield aliphatic methine and eight methines in the aromatic-vinyl region of the spectrum.

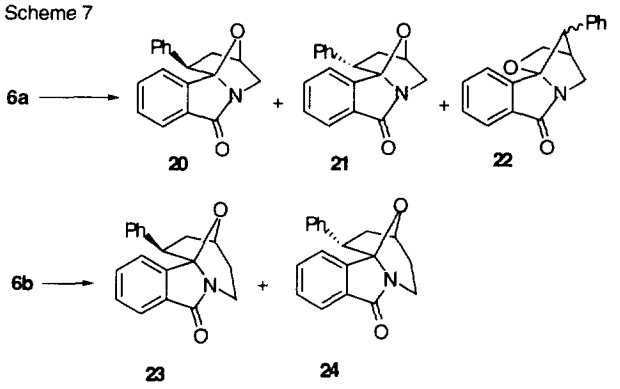
The formation of photoproducts **17**, **18**, and **19** can be rationalized as arising by an electron transfer reaction between the imide and cyclopropyl portions of the molecule (Scheme 6) to afford the radical anion/radical cation followed by imide oxygen attack on the cyclopropyl ring to form an intermediate biradical (**25**) with a 5-membered (n=1) or 6-membered ring (n=2). Radical-radical coupling yields photoproducts **17** and **18**. However, in intermediate **25** (n=2), if an hydrogen atom is abstracted *via* a 5-membered transition state, then terminal olefin **19** is produced. Isolation of olefin **19** provides further evidence to support the proposed stepwise mechanism for this type of reaction.

Scheme 6



Photolysis (Scheme 7) of the 1,2-substituted cyclopropyl imide **6a** afforded two types of heterocycles--the diastereomeric oxazolidines **20** and **21** and a 1,3-oxazine **22**. The relative stereochemistry of the phenyl group of isomers **20** and **21** was assigned based on previous results[2a] for the intermolecular reaction products **1** and **2**. It was shown that the N-methyl signal in the proton NMR for the syn isomer, **1**, is shifted upfield due to the anisotropic effects of the phenyl group relative to that for the anti isomer.

Scheme 7



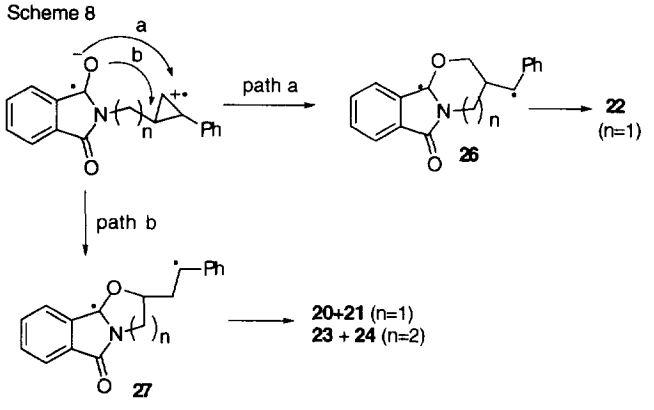
Examination of the NMR for the 1,3-oxazine **22** showed two 1H multiplets at δ 4.05 and 4.37, which were coupled to each other, indicating a diastereotopic methylene adjacent to an oxygen atom. In addition, two 1H multiplets at δ 3.61 and 3.85, also coupled to each other, pointed to a methylene group adjacent to the lactam nitrogen.

Photolysis of imide **6b** produced the two isomeric spirolactams **23** and **24** in approximately an 1:1 ratio. The structures of these photoadducts was readily deduced by examination of the proton and carbon NMR. Both showed a 1H multiplet at about δ 5 for the

proton adjacent to the oxygen, as well as the multiplets indicative of the diastereotopic methylene adjacent to the lactam in the region of δ 3.5-4.4.

The mechanism for the formation of photoproducts **20-24** is depicted in Scheme 8. Electron transfer affords the radical cation/radical anion pair. Nucleophilic attack of the imide radical anion onto the phenylcyclopropane radical cation can occur *via* two pathways. Pathway "a" leads to formation of a 6-membered biradical **26** (n=1). Coupling of intermediate **26** leads to the formation of **22**. If attack occurs *via* pathway "b", then biradical **27** is formed. Radical-radical coupling affords photoproducts **20**, **21**, **23**, and **24**.

Scheme 8



Conclusions

The results presented here provide additional evidence that the intermolecular or intramolecular photochemical reaction of aromatic imides with phenylcyclopropanes proceeds *via* electron transfer. Furthermore, the isolation of olefin **19** supports previous experiments[2] which demonstrated that the nucleophilic attack of the radical anion onto the radical cation is a stepwise mechanism rather than a concerted one.

Experimental

General. Melting points are uncorrected. Irradiations were carried out in Pyrex test tubes with a 450-W Hanovia medium-pressure mercury lamp. Proton and carbon NMR were recorded at 400 and 100 MHz, respectively.

1-Phenylcyclopropylmethanol (8). 1-Phenylcyclopropanecarboxylic acid **(7)** was reduced with lithium aluminum hydride according to the procedure of Mazzocchi and Lustig.[3] ^{1}H NMR ($CDCl_3$) d 7.19-7.37 (m, 5H), 3.66 (s, 2H), 1.60 (s, 1H, exchangeable), 0.80-0.92 (m, 4H).

2-Phenylcyclopropylmethanol (10). This was prepared in a manner similar to **8** and has spectral data identical to that reported in the literature.[8]

N-(1-Phenylcyclopropylmethyl)phthalimide (5a). To phthalimide (270 mg; 1.84 mmol), 1-phenylcyclopropylmethanol (213 mg; 1.44 mmol), and triphenylphosphine (492 mg; 1.88 mmol) in anh THF (20 mL), was added DEAD (0.30 mL; 1.91 mmol) in anh THF (5 mL) under a nitrogen atmosphere at room temperature. The reaction was heated at reflux temperature overnight. After cooling, the solvent was evaporated and the residue chromatographed on silica gel using 15% EtOAc/hexanes. Isolated as colorless needles, mp=102-103°C (EtOH). ^{1}H NMR ($CDCl_3$) δ 7.60-7.80 (m, 4H), 7.05-7.25 (m, 5H), 3.87 (s, 2H), 1.05 (m, 2H), 0.86 (m, 2H). IR 1765, 1710 cm^{-1}. MS 277 (MH^+). HRMS calcd for $C_{18}H_{15}NO_2$: 277.1103. Found: 277.1113.

N-(2-Phenylcyclopropylmethyl)phthalimide (6a). This was prepared in a manner analogous to phthalimide **5a** utilizing alcohol **10** in the Mitsunobu reaction and was isolated as colorless needles, mp=72-73°C (EtOH). ^{1}H NMR ($CDCl_3$) δ 7.60-7.80 (m, 4H), 7.00-7.30 (m, 5H), 3.62 (d, J=9.0 Hz, 2H), 0.80-2.20 (m, 4H). IR 1760, 1705 cm^{-1}. MS 277 (MH^+). HRMS calcd for $C_{18}H_{15}NO_2$: 277.1103. Found: 277.1100.

2-(1-Phenylcyclopropyl)ethyl acetate (12). Zinc dust (222.5 mg, 3.403 mmol) and copper (I) chloride (334.2 mg, 3.376 mmol) in anhydrous ether (6 mL) were refluxed under a nitrogen atmosphere for 1 h. 3-Phenylbut-3-en-1-yl acetate **(11)**[5] (170.7 mg, 0.8984 mmol) in ether (3 mL) and methylene iodide (0.35 mL, 4.34 mmol) were added. Reflux was continued for 70 h. The suspension was filtered through a pad of Celite and the filtrate was extracted with HCl (1N, 2 x 30 mL). The organic layer was washed with water (30 mL), dried ($MgSO_4$), filtered and evaporated. Purification by chromatography afforded cyclopropyl ester **12** as a clear oil with spectral properties identical to those reported by Perkins[6] (101.3 mg, 55% yield). ^{1}H NMR ($CDCl_3$) δ 7.20-7.40 (m, 5H), 4.04 (t, J=7.2 Hz, 2H), 1.95 (s, 3H), 1.90 (t, J=7.2 Hz, 2H), 0.70-0.87 (m, 4H). IR 1735, 1240 cm^{-1}.

2-(1-Phenylcyclopropyl)ethanol (13). Cyclopropyl ester **12** (608.8 mg, 2.984 mmol) and KOH (0.2N, 20 mL) in methanol (40 mL) were heated at reflux temperature for 5 h. After cooling, the reaction was poured into water (40 mL) and extracted with methylene chloride (3 x 75 mL). The combined organic layers were washed with water (50 mL), dried (Na_2SO_4), filtered and evaporated. The residue was chromatographed on a small silica gel column (15% ethyl acetate/hexanes) to provide alcohol **13** as a clear oil (447.5 mg, 93% yield). The spectral properties were identical to those reported by Wilt[9]. ^1H NMR ($CDCl_3$) δ 7.17-7.34 (m, 5H), 3.62 (t, J=6.9 Hz, 2H), 1.85 (t, J=6.9 Hz, 2H), 0.72-0.85 (m, 4H). IR 3624, 3000-3100 (br), 1602, 1424 cm^{-1}.

2-(1-Phenylcyclopropyl)ethyl choride (14). Alcohol **13** (447.5 mg, 2.779 mmol) and triphenylphosphine (963.3 mg, 3.672 mmol) were refluxed in carbon tetrachloride (100 mL) under a nitrogen atmosphere for 2 days. The suspension was filtered through a pad of Celite and the filtrate evaporated. Chromatography using a small silica gel column (hexanes) afforded chloride **14** as a clear oil (477.3 mg, 95% yield). ^1H NMR ($CDCl_3$) δ 7.19-7.33 (m, 5H), 3.43 (t, J=7.6 Hz, 2H), 2.02 (t, J=7.6 Hz, 2H), 0.74-0.89 (m, 4H). IR 3081, 1451 cm^{-1}.

N-[2-(1-Phenylcyclopropyl)ethyl]phthalimide (5b). Potassium phthalimide (131.6 mg, 0.710 mmol) and the cyclopropyl chloride **14** (85.6 mg, 0.475 mmol) were heated at 130°C in anh DMF (10 mL) for 5 h. The yellow solution was poured into water (30 mL) and washed with chloroform (3 x 30 mL). The combined organic layers were washed with water (20 mL), dried ($MgSO_4$), filtered and evaporated. Pure alkylated phthalimide **5b** was obtained upon flash chromatography (silica gel, 5% ethyl acetate/hexanes) as a clear oil (93.2 mg, 67% yield). ^1H NMR ($CDCl_3$) δ 7.63-7.80 (m, 4H), 7.05-7.37 (m, 5H), 3.66-3.73 (m, 2H), 1.96-2.04 (m, 2H), 0.75-0.91 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 168.2, 143.8, 133.9 (CH), 132.2, 128.3 (CH), 128.2 (CH), 125.9 (CH), 123.0 (CH), 37.9 (CH_2), 36.4 (CH_2), 23.4 (CH_2), 13.4 (CH_2). IR 1772, 1712, 1398 cm^{-1}. HRMS calcd. for $C_{19}H_{17}NO_2$: 291.1259. Found: 291.1233.

Trans N-(4-Phenyl-3-butenyl)phthalimide (16). Potassium phthalimide (2.30 g, 12.41 mmol), 4-bromo-1-phenyl-1-butene **(15)**[7] (2.3052 g, 10.93 mmol) and a catalytic amount of tetrabutylammonium bromide were heated at reflux in benzene (50 mL) under a nitrogen atmosphere for 24 h. After cooling, the reaction was filtered through a pad of Celite and the pad thoroughly washed with methylene chloride. The organic filtrate was evaporated and the residue purified by silica gel chromatography (5% ethyl acetate/hexanes) to afford product **16** as a white

solid (2.73 g, 90% yield; mp=133.5-135.5°C). ^{1}H NMR ($CDCl_3$) δ 7.67-7.89 (m, 4H), 7.16-7.32 (m, 5H), 6.39-6.51 (m, 1H), 6.16 (dt, J=15.7, 6.9 Hz, 1H), 3.84 (t, J=6.9 Hz, 2H), 2.61 (ddt, J=1.2, 6.9, 6.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 168.3, 137.4, 133.8 (CH), 132.6 (CH), 132.2, 128.4 (CH), 127.2 (CH), 126.2 (CH), 126.1 (CH), 123.2 (CH), 37.6 (CH_2), 32.2 (CH_2). IR 1710, 1390 cm^{-1}. HRMS calcd. for $C_{18}H_{15}NO_2$: 277.1099. Found: 277.1104.

N-[2-(2-Phenylcyclopropyl)ethyl]phthalimide (6b). Alkylated phthalimide **16** (923.7 mg, 3.33 mmol) in anhydrous benzene (25 mL) was added to diethyl zinc (1M solution in ether, 24.0 mL) under a nitrogen atmosphere and the resulting solution was heated to reflux temperature. Methylene iodide (2.0 mL, 24.8 mmol) was added dropwise over a 35 minute period. After refluxing for 60 h, the solution was poured into HCl (0.1N, 250 mL). The aqueous layer was extracted with methylene chloride (3 x 200 mL). The combined organic layers were washed with saturated $NaHCO_3$ (100 mL), water (100 mL), dried ($MgSO_4$), filtered and evaporated to give a mixture of starting material **16** and cyclopropyl product **6b**. Since these were inseparable using conventional methods, the mixture was reacted with ozone (CH_2Cl_2, -78°C, Me_2S) and then chromatographed on silica gel (5% ethyl acetate/hexanes) to afford product **6b** (122.5 mg, 21% yield) as a white solid (mp=75-76°C). ^{1}H NMR ($CDCl_3$) δ 7.65-7.90 (m, 4H), 6.90-7.25 (m, 5H), 3.83 (m, 2H), 1.65-1.90 (m, 2H), 1.56-1.65 (m, 1H), 1.05-1.12 (m, 1H), 0.75-0.93 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 168.4, 142.9, 133.7 (CH), 132.2, 128.1 (CH), 125.5 (CH), 125.2 (CH), 123.1 (CH), 37.7 (CH_2), 32.9 (CH_2), 22.9 (CH), 20.7 (CH), 15.4 (CH_2). IR 1710, 1395 cm^{-1}. HRMS calcd. for $C_{19}H_{17}NO_2$: 291.1259. Found: 291.1255.

General Procedure for the Irradiation of Phthalimides 5 and 6.
Alkylated phthalimide **5** or **6** in benzene (45 mL) in a Pyrex test tube was purged with nitrogen and irradiated for the indicated length of time. After the benzene was evaporated, the residue was chromatographed on a silica gel column (ethyl acetate/hexanes) to provide the photoproducts.

Photolysis of phthalimide 5a. Irradiated for 5 hours. Spiro adduct **17** was isolated as a colorless oil (7%, 42% based on recovered starting material). ^{1}H NMR ($CDCl_3$) δ 7.25-7.95 (m, 9H), 3.62 (d, J=9.4 Hz, 1H), 3.55 (dd, J=9.4, 2.4 Hz, 1H), 2.30-2.59 (m, 4H). IR 1700 cm^{-1}. MS 277 (MH^+). HRMS calcd. for $C_{18}H_{15}NO_2$: 277.1103. Found: 277.1100.

Photolysis of phthalimide 5b. Irradiated for 4 hours. The more polar photoproduct **18** was isolated as a white solid (52.2 mg, 61% yield; mp=159-161°C). ^{1}H NMR ($CDCl_3$) δ 7.50-7.90 (m, 4H), 7.25-7.47 (m, 5H), 4.41 (ddd, J=1.4, 6.3, 13.7 Hz, 1H), 3.50 (ddd, J= 5.7, 11.6, 13.7 Hz, 1H), 2.55-2.70 (m, 2H), 2.35-2.50 (m, 1H), 2.25-2.33 (m, 1H), 1.88-2.05 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 164.6, 144.7, 142.1, 133.4, 131.8 (CH), 130.0 (CH), 128.4 (CH), 127.3 (CH), 124.4 (CH), 123.6 (CH), 122.2 (CH), 94.4, 85.9, 36.3 (CH_2), 34.9 (CH_2), 34.3 (CH_2), 34.2 (CH_2). IR 3060, 1693, 1423 cm^{-1}. HRMS calcd. for $C_{19}H_{17}NO_2$: 291.1259. Found: 291.1237. The minor olefinic photoproduct **19** was isolated as a clear oil (6.1 mg, 7% yield). ^{1}H NMR ($CDCl_3$) δ 7.40-8.00 (m, 4H), 7.15-7.50 (m, 5H), 6.14 (ddd, J=1.1, 11.0, 17.8 Hz, 1H), 6.02 (br s, 1H), 5.68 (d, J=11.0 Hz, 1H), 5.55 (d, J=17.8 Hz, 1H), 4.38 (ddd, J=1.7, 5.7, 13.2 Hz, 1H), 3.52 (dt, J=3.7, 13.2 Hz, 1H), 2.37 (ddd, J=1.7, 3.7, 14.0 Hz, 1H), 1.94 (dddd, J=1.1, 5.7, 13.2, 14.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 166.2, 144.6, 142.2, 139.2 (CH), 132.9, 131.7 (CH), 129.8 (CH), 128.3 (CH), 127.3 (CH), 124.9 (CH), 123.7 (CH), 123.3 (CH), 118.8 (CH_2), 80.4 (CH), 79.9, 35.3 (CH_2), 33.1 (CH_2). IR 1696, 1432 cm^{-1}.

Photolysis of phthalimide 6a. Irradiated for 1 hour to afford starting material (20 mg) as well as three photoadducts **20-22.** Diastereomers **20** and **21** were isolated as a 3:1 mixture (colorless oil, 40% yield, 47% yield based on recovered starting material). Major isomer **20**: ^{1}H NMR ($CDCl_3$) δ 7.00-7.80 (m, 8H), 6.00 (m, 1H), 5.23 (dd, J=5.3, 4.2 Hz, 1H), 3.51 (m, 1H), 3.47 (dd, J=9.2, 5.4 Hz, 1H), 3.19 (d, J=8.3 Hz, 1H), 2.49 (dd, J=12.5, 8.5 Hz, 1H), 2.32 (m, 1H). IR 1680 cm^{-1}. Diastereomer **21**: ^{1}H NMR ($CDCl_3$) δ 7.00-7.80 (m, 9H), 5.20 (dd, J=5.5, 4.1 Hz, 1H), 3.85 (dd, J=11.5, 5.3 Hz, 1H), 3.67 (ddd, J=9.6, 4.1, 2.4 Hz, 1H), 3.36 (d, J=9.6 Hz, 1H), 2.69 (dddd, J=12.6, 11.6, 5.5, 2.4 Hz, 1H), 2.00 (dd, J=12.6, 5.3 Hz, 1H). IR 1680 cm^{-1}. HRMS calcd. for $C_{18}H_{15}NO_2$: 277.1103. Found: 277.1081 (mixture of diastereomers). Photoadduct **22** was isolated as a colorless oil, 19% yield, 22% yield based on recovered starting material. ^{1}H NMR ($CDCl_3$) δ 7.80 (m, 1H), 7.30-7.65 (m, 8H), 4.37 (ddd, J=8.2, 3.7, 3.0, 1H), 4.05 (d, J=8.2 Hz, 1H), 3.85 (ddd, J=10.0, 3.7, 3.0 Hz, 1H), 3.61 (d, J=10.0 Hz, 1H), 3.13 (m, 1H), 3.04 (s, 1H). IR 1680 cm^{-1}.

Photolysis of phthalimide 6b. Irradiated for 45 minutes to yield starting material (37.5 mg) and the two diastereomeric photoproducts **24** and **23** in 39% and 44% isolated yield respectively as they were eluted from the column. The less polar isomer (39%) was isolated as a white solid

(mp=112-115°C). ^{1}H NMR ($CDCl_3$) δ 7.51-7.79 (m, 4H), 6.89-7.15 (m, 5H), 4.92 (m, 1H), 4.21 (dd, J=13.9, 7.2 Hz, 1H), 4.08 (dd, J=11.9, 7.2 Hz, 1H), 3.31 (ddd, J=13.8, 11.8, 5.6 Hz, 1H), 2.95 (dt, J=7.8, 12.3 Hz, 1H), 2.49 (ddd, J=12.9, 7.3, 1.0 Hz, 1H), 2.04-2.16 (m, 1H), 1.62 (ddd, J=13.5, 5.5, 1.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 165.9, 142.1, 135.5, 133.6, 131.9 (CH), 130.1 (CH), 128.4 (CH), 127.1 (CH), 127.0 (CH), 123.8 (CH), 121.8 (CH), 95.8, 75.5 (CH), 50.4 (CH), 34.0 (CH_2), 31.8 (CH_2), 28.7 (CH_2). IR 3000, 1690, 1410 cm^{-1}. HRMS calcd. for $C_{19}H_{17}NO_2$: 291.1259. Found: 291.1278 (mixture of both diastereomers). The more polar isomer was isolated as a white solid (mp=138-138.5°C). ^{1}H NMR ($CDCl_3$) δ 7.70-7.78 (m, 1H), 7.00-7.37 (m, 7H), 6.10 (m, 1H), 5.01 (br s, 1H), 4.39 (dd, J=13.8, 6.6 Hz, 1H), 3.59 (t, J=6.6 Hz, 1H), 3.51 (ddd, J=13.8, 12.1, 5.0 Hz, 1H), 2.69-2.74 (m, 2H), 2.10 (dddd, J=13.1, 12.1, 6.6, 3.1 Hz, 1H), 1.64 (ddd, J=13.1, 5.0, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 164.8, 142.2, 140.4, 133.1, 130.8 (CH), 129.4 (CH), 128.8 (CH), 128.4 (CH), 127.4 (CH), 124.0 (CH), 122.9 (CH), 96.7, 75.3 (CH), 52.9 (CH), 36.5 (CH_2), 33.3 (CH_2), 28.8 (CH_2). IR 2980, 1690, 1410 cm^{-1}.

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